DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

U. S. GOVERNMENT CONTRACT DA-44-109-QM-64

PROGRESS REPORT

FOR THE PERIOD

JUNE 5, 1952 to OCTOBER 6, 1952

REPORT No. 13

CONNECTICUT HARD RUBBER COMPANY

NEW HAVEN, CONNECTICUT

THE CONNECTICUT HARD RUBBER COMPANY, NEW HAVEN, CONNECTICUT

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Progress Report for the Period

June 5, 1952 to October 6, 1952

March 13, 1953

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ASSIGNMENT

Taken from Contract No. DA-44-109-QM-64 dated November 28, 1949.

1. Conduct a series of fundamental studies on the reinforcement of rubber by the treatment of currently available rubber carbon blacks and other reinforcing pigments to make them compatible with silicone-type polymers.

2. The selection and development of a catalytic condensing composition that will work on the pigment-reinforced system referred to in (1) above.

3. Modification of the fundamental characteristics of the present polymer so as to produce greater chain length and the modified cross linkages necessary for greater strength.

Taken from Modification "C", dated October 4, 1950

4. Pursue new developments on the liquefaction of silicone rubbers by the use of anhydrous acids and their repolymerization after adding fillers.

5. Obtain improved polymers of silicone, particularly by the utilization of the hydrolysis of the alkylchlorosilanes with a combination of water and alcohols of various types.

6. Study new methods of cross-linking to produce better silicone polymers.

7. Continue the study, development and test of methods to improve the reinforcement of silicone rubber and the polymer itself to obtain desired low-temperature characteristics.

ASSIGNMENT (Cont.)

Taken from Modification "E", dated September 21, 1951

8. Study extensively methods of silicone vulcanization, including types of vulcanizing agents. (Such methods as preconditioning of uncured stocks boosted up the tensile strength and ultimate elongation.) Vulcanizing agents, other than PbO_2, should be investigated.

9. Investigation, in detail, surface effects of pigments with particular emphasis on pH relation to physical properties. (Alon, for example, gives the best reinforcement when it is acidic with a narrow range of pH around 5.4 . Other pigments should be investigated.)

10. Introduce reactive groups at high temperatures in air and in presence of chemical oxidizers such as chromates, permanganates, etc.

11. Follow any practical and special applications which show promise, growing out of the contract, at least to the point of proving whether they are of value or not. (As an example, one of the special applications developed in the present contract is the use of ammonia-stabilized, depolymerized, flex-resistant silicone adhesive in diaphragms for diffusion apparatus for atomic work.)

SUMMARY

1. The following pigments were tested for reinforcing properties in General Electric SE-76: Celite 270, Celite Superfloss, a special alumina aerogel (Monsanto), Monsanto Silica N, Syton SPR 5435, Santocel K233F and Burgess Iceberg (calcined aluminum silicate). Of these pigments, Celite 270, Celite Superfloss and Burgess Iceberg had moderate reinforcing properties and would be useful as diluents in conventional silicone rubber compounds. The others had no outstanding properties.

2. It was demonstrated that by heating SE-76 silicone gum at 300° and 480°F. that 8 and 17 percent, respectively, of the polymer is distilled off. This results in slightly diminished tensile, considerable loss in elongation and corresponding increase in hardness when the residual rubber is compounded. It would appear that in the usual long oven cure some of the volatile silicones are removed by distillation.

3. The effect of a variation in molecular weight of silicone rubber from approximately 400,000 to 800,000 when this rubber is compounded with Santocel C and benzoyl peroxide appears to be small. The lower molecular weight rubber is much more easily handled on the mill in that it bands on the rolls easier with less tendency to fall apart.

4. With recipes containing benzoyl peroxide, carrying out the press curing operation at 200 or 210°F. for 10 minutes resulted in a slight improvement in the physical properties of the recipes after oven curing. A 10-minute cure at 210°F. is the recommended press cure.

5. Preheating a carbon black, silicone rubber master batch for 16 hours at 400°F. before adding the curing agent had the result of improving the physical tests when tertiary butyl perbenzoate was used as a curing agent. The results were not high, (tensile 250 p.s.i.) indicating that carbon black does not reinforce silicone rubber appreciably.

6. Similar preheating experiments with a special titanium dioxide (Titanox MP-561-6) had no noticeable effect. This pigment had a moderate reinforcing effect.

7. An attempt was made to secure high-temperature stability with Du Pont GS199S Silica-reinforced compounds by introducing benzoyl peroxide as an additional curing agent. These compounds overcured at 480°F. as usual, becoming brittle. Compounds containing no benzoyl peroxide were slightly more heat-resistant than those containing benzoyl peroxide.

8. There was no improvement in the above compounds as a result of using 210°F. as a press curing temperature instead of higher temperatures.

9. With a low-molecular-weight silicone rubber, oven curing at 300°F. failed to effect the optimum cure in 96 hours when 25 percent GS199S Silica was used. At 400°F., the optimum cure was approximately 6 hours, and at 450°F. the optimum was less than 1 hour. Good low-compression-set values were not reached before 24 hours at 400°F., at which time the elongation had dropped to 100 percent.

10. Experiments were conducted to study the effect of variation of molecular weight on the physical properties obtained with GS199S Silica as the sole curing agent. There is a definite improvement in the tensile strength when gum of a molecular weight above 600,000 is used. There is not much effect on elongation and there is only a slight effect on the stiffness or modulus. The large increase in tensile occurs at the end of the stress-strain curve and may attain a value which is double the tensile value for gums of half the molecular weight.

11. Special samples of GS199S Silica with smaller amounts of organic coating proved to have no outstanding properties. In the absence of coating, only 10 volumes of GS Silica could be incorporated in the rubber.

12. GS199S Silica, dried over a desiccant, appeared to have slightly increased reinforcing action and slightly improved high-temperature-curing resistance.

13. GS199S Silica with the coating removed by heating in air, had very inferior reinforcing and curing action. When the coating was removed by heating in a vacuum, the loss in weight was only 4 percent, and the pigment lost no curing activity and showed a slight improvement in resistance to high-temperature cure. When the GS199S Silica concentration was reduced to 10 percent, compounds withstood curing at 480°F. for 16 hours. This is a means of controlling curing activity of the silica, but the reinforcing action was greatly reduced, especially in low-molecular-weight gum.

14. It was found possible to create resistance to high-temperature curing (24 hours at 400° + 9 hours at 480°F.) by remilling or freshening the mixed batches three times on successive days. By this means, one 25-volume compound was produced which had the following properties:

Tensile 800, Elongation 375, Hardness 75

This was obtained with a low-molecular-weight gum. The addition of a preheating step to the remilling operation had no beneficial effect.

15. Special press curing techniques such as removing the slab from the mold while hot had no beneficial effect on the high-temperature-curing properties. Confining the GS199S Silica compound in a mold during oven curing had no beneficial effect. In the case of a benzoyl peroxide recipe, curing in a mold in the oven depolymerized the stock.

16. Silicone oil, glycerol-stabilized, depolymerized silicone gum and seven commercial plasticizers, of which tricresyl phosphate is an example, had no beneficial effect on high-temperature resistance.

17. Soaking cured slabs in a benzene solution of silicone oils or silicone gum did not serve to plasticize brittle oven-cured slabs.

18. Free radical inhibitors such as sodium nitrite, quinoline, sulfur, diphenyl amine, and stearic and benzoic acids in one percent quantities did not improve brittleness caused by high-temperature curing.

19. Mixtures of GS199S Silica with Santocel C and with Alon did not result in stocks which were free from brittleness when cured at high temperatures.

20. A study of the polymerization or vulcanization of hexamethyldisiloxane by heating with chlorobenzoyl peroxide indicated that 28 percent of the peroxide was transformed into chlorobenzoic acid with the formation of polymeric molecules. The balance of the peroxide appears to substitute on the methyl side chains partly as phenyl and partly as benzoyl groups. Only 16 percent of the hexamethyldisiloxane was polymerized.

21. Direct analysis of cured slabs of silicone rubber showed only 4 to 10 percent of the benzoyl peroxide ending up in the form of benzoic acid. Over 75 percent of the benzoyl

peroxide is decomposed with a 5-minute rise to 212° plus 10 minutes at 212°F., or with a 10-minute rise to 230° plus 5 minutes at 230°F. There would appear to be no reason for press cures longer than those indicated above, nor for benzoyl peroxide concentrations higher than 2 percent (unless one is dealing with very low-molecular-weight silicone, such as an oil).

RECOMMENDATIONS

1. It is recommended that the Government continue to encourage and support investigations concerned with the reinforcement of silicone rubber, with particular emphasis on further evaluation of DuPont GS Silica.

2. Since the subject contract is completed, it is recommended that the Company continue studies of pigment-reinforcement and vulcanization of silicone rubber because it is probable that further research will eventually result in further improvements in silicone compounds with respect to strength and rubberiness. Such improvements will bring with them improved tear and abrasion-resistance, and these, together with the well-known heat and cold-resistance of the polymer, will make the silicones severalfold more useful in the future.

INTRODUCTION

The testing of new pigments for silicone rubber has been continued in this period. No new outstanding pigments were uncovered during the period covered by this report.

Further study of the effect of the temperature of press curing has been made. Since primary cross linking occurs in this short interval, the temperature and time of press curing are important variables which should be carefully controlled.

The behavior of SE-76 polymer upon heating has been studied to see if low-molecular-weight products cause low tensile strength in GS199S Silica recipes. The effect of the molecular weight of the polymer on the physical properties obtained with Santocel-C reinforced or GS199S Silica reinforced stocks has been studied.

Since a major problem in the use of GS199S Silica has been a lack of stability at 300-480°F., many attempts have been made, reported herein, to find a combination which would withstand high-temperature curing and aging. Variation in press curing time and temperature, variation in oven curing time and temperature, preheating the gum, preheating the pigment, remilling the mixed compound, plasticizing the compound, reduction of the degree of coating on the pigment, curing in a mold instead of in an oven, and other variations of procedure have been tried in an attempt to achieve high-temperature stability. All of these studies are reported in this report (No. 13).

Further studies of the mechanism of vulcanization by peroxides have been conducted. It is apparent that the primary reaction is a simple metathesis occurring between a dissolved benzoyl peroxide molecule and two adjacent methyl side chains:

$$2\ \vdots Si-CH_3 + (C_6H_5COO)_2 \longrightarrow \vdots Si-CH_2-CH_2-Si\vdots + 2\ C_6H_5COOH$$

Side reactions occur in which benzoyl or phenyl groups replace hydrogen. Substitutions, or other side reactions, occur to a greater extent as the benzoyl peroxide concentration is increased, thus decreasing the efficiency of the curing agent.

Special attention is called to the rate of cure studies of GS199S-cured recipes in Figure II-A-3. It was found that the low-molecular weight gum Batch 11317 could be cured practically indefinitely in an oven at 300° F. (up to 90 hours) without the development of excessive stiffness or brittleness. At 400° F., however, equivalent results are obtained only with a very short cure in the oven (four to ten hours) because beyond this period an excessive cross linking action occurs resulting in very stiff, low-elongation compounds. As noted elsewhere in this report, at 480° F. the stiffening or embrittling reaction is much more rapid.

The final date of the contract was October 6, 1952. Experimental work was continued up to and even beyond this date in an effort to seek some elusive answers, especially with reference to high-temperature curing with GS 199S Silica. This and the Final Summary Report are therefore being written after the termination of the contract.

PROGRAM

This contract has extended over a period of three years, and the detailed experimental program has changed (with the approval of Dr. Juan Montermoso and others of the Office of the Quartermaster General) several times as the work has progressed. The most recent program has been as follows:

1. Continue compounding experiments with new pigments as reinforcing agents for SE-76 rubber.
2. Heat SE-76 polymer and determine if improved reinforcement is obtained.
3. Determine molecular weights of all samples of SE-76 and compare the tensiles obtainable with GS199S Silica with the molecular weight of the polymer.
4. Make a further study of the effect of press curing temperature on the physical properties obtained when curing with benzoyl peroxide.
5. Try the "preheating" technique with Micronex and finely divided Titanium Dioxides to see if improved curing characteristics will result.
6. Vary the press curing temperature and oven curing time and temperature to see if there is some set of conditions which will give improved high-temperature resistance to GS199S Silica compounds in SE-76 rubber.
7. Test GS Silica samples with varying degrees of coating.

PROGRAM (Cont.)

8. Heat GS199S Silica to remove or destroy the coating and evaluate the heated pigments.
9. Study the effect of remilling GS199S Silica compounds to see if high-temperature curing results are improved.
10. Study the plasticizing action of several plasticizers in GS199S Silica compounds to see if high-temperature curing properties are improved.
11. Vulcanize hexamethyldisiloxane with p-chlorobenzoyl peroxide. Isolate fractions of increased molecular weight. Analyze products to find disposition of the p-chlorobenzoyl peroxide.
12. Measure the rate of decomposition of benzoyl peroxide during press curing and the rate of appearance of benzoic acid.
13. Write Quarterly Report No. 13.

TABLE I-A-1

Evaluation of Celite Pigments

Compound No.	Pigment	Vol.% of Pigment	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2325	Celite 270 (fine)	15	272	150	32	---	---
2325-1		25	497	162	47	---	---
2325-2		40	532	100	62	---	---
2307	Celite Superfloss	15	229	250	28	160	---
2307-1		25	327	283	39	225	---
2307-2		40	417	162	60	---	---

TABLE I-A-2

Celite Pigments as Diluents for Santocel C

Compound No.	Pigment	Vol.% of Pigment	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2309	Santocel (Control)	15	818	275	43	500	---
2309-1	Plus 20% Celite Superfloss	15	807	262	50	550	---
2309-2	Plus 40% Celite Superfloss	15	604	200	51	604	---
2309-3	Plus 20% Celite 270	15	636	200	48	600	---
2309-4	Plus 40% Celite 270	15	539	212	53	515	---

Footnotes:

(1) General Electric SE-76 silicone gum used, with 2.0% benzoyl peroxide as curing agent.
(2) Press Cure 15 minutes at 230°F.
(3) Oven Cure 1 hour at 300°F.

I. REINFORCEMENT OF SILICONE RUBBER.

A. New Pigments in General Electric SE-76 Gum.

1. Evaluation of Celite Pigments.

Celite 270 is a special fine grind of diatomaceous earth pigment supplied by the Johns-Manville Company. Its properties in compounding at various loadings are given in Table I-A-1 and are compared with Celite Superfloss which has been evaluated earlier. Reinforcement is greater with the 270 at similar volume loadings, and this pigment resembles Santocel C in producing a higher tensile, lower elongation and harder stock. Its price of $.06 per pound is considerably less than that of Santocel C. It does not have outstanding reinforcing properties, but could be used as an extender or diluent. It is said to be far better than Santocel C for water resistance of its silicone compounds.

2. Celite Pigments as Diluents for Santocel C.

Superfloss is recommended as an additive to increase the durometer of General Electric SE-450 stock. This is a Santocel C stock, so it was of interest to compare the diluting effects of Celite Superfloss and the new 270. Data given in Table I-A-2 indicate that addition of Celite 270 or Superfloss to a 15 volume Santocel C compound can be made satisfactorily up to 40 per cent by weight with a durometer increase of only 10 points. This fine grind diatomaceous earth is practically as good a diluent as the standard Superfloss, which is the standard pigment for this purpose.

3. Aluminum Oxide Aerogel.

The Monsanto Chemical Company supplied us with a small sample of experimental alumina aerogel for evaluation. This alumina aerogel was similar in appearance and structure to the silica aerogel "Aerosil" which was tested earlier and was presumably made from an aluminum hydroxide gel by the Kistler process. It was a nearly pure alumina of low density and very high porosity, so that it would break up easily on the mill to produce finely-divided, porous material. It differs from the finely-divided alumina Alon in that Alon consists of fine, non-porous particles.

A comparison of this alumina aerogel with Alon is shown in Table I-A-3. Both compounds were preheated 1 hour at 300°F. before addition of peroxide and curing in accordance with our previous experience. During the preheating, the alumina aerogel compound lost 5.5 per cent and the Alon 5.3 per cent in weight, indicating equivalent evaporation of low molecular weight polymer. The alumina aerogel batch cured satisfactorily, but gave a hardness of only 30 with a tensile strength of 186 p.s.i. Since this pigment is highly porous, one would expect greater absorption of polymer with a higher hardness, similar to Santocel. However, this was not the case, and it is probable that the alumina was not reduced to a sufficiently small particle size on the mill. In view of the excellent reinforcing properties of Alon, it would be of interest to do further work with porous alumina of this type when it is available.

4. <u>Monsanto Silica Pigments.</u>

Table I-A-4 gives data on four experimental silica pigments supplied by the Monsanto Chemical Company during this period.

TABLE I-A-3

Evaluation of Alumina Aerogel Pigment

Compd. No.	Pigment	Vol.% of Pigment	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2273	Alumina Aerogel	15	186	788	38	87	124
2274	Alon C-52 (Control)	15	354	700	42	160	265

Footnotes:
(1) Gen.Elec. SE-76 silicone gum used, with 3.0% benzoyl peroxide as curing agent.
(2) Press cure 15 minutes at 230°F.
(3) Oven cure 1 hour at 300°F.
(4) Batches preheated 1 hour at 300°F. before addition of peroxide and curing.
(5) Weight loss of 2273 during preheat = 5.5 per cent.
" " " 2274 " " = 5.3 " "

TABLE I-A-4

Evaluation of Monsanto Silica Pigments

Compd. No.	Pigment	Vol.%	Oven Cure	Tensile Strength p.s.i.	Elong. Percent	Hard. Shore A	St.@ 200%	St.@ 400%
2375	Silica N	10	1 hr. @ 300°F. 24 hrs. @ 400°F.	56	700 No Cure	7	---	---
2375-1		20	1 hr. @ 300°F. 24 hrs. @ 400°F.		No Cure No Cure			
2376	Syton SPR 5453	10	1 hr. @ 300°F. 24 hrs. @ 400°F.	41	750 No Cure	4	---	---
2376-1		20	1 hr. @ 300°F. 24 hrs. @ 400°F.	53	763 No Cure	11	---	---
2421	Santocel K233F	20	1 hr. @ 300°F.	64	100	38	---	---
2422	I-P-3	20	1 hr. @ 300°F.	83	300	23	---	---

Footnotes:
(1) Gen.Elec. SE-76 silicone gum used, with 2.0% benzoyl peroxide as curing agent.
(2) Press cure of 15 minutes at 230°F.; oven cure as indicated.

TABLE I-A-5

Evaluation of Burgess Iceberg Pigment at Varying Cures

Compd. No.	Pigment	Wt.% Pigment	Oven Cure	Tensile Strength p.s.i.	Elong. Percent	Hard. Shore A	St.@ 200%	St.@ 400%
2352 (A)	Iceberg	80	3 hrs. @ 300°F.	398	213	39	392	---
(B)			16 hrs. @ 400°F.	389	150	42	---	---
(C)			16 hrs. @ 400°F. + 16 hrs. @ 480°F.	478	113	57	---	---

Footnotes:
(1) Gen.Elec. SE-76 gum used, with 2.0% benzoyl peroxide as curing agent.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

Properties and composition of these silicas were not available; however, a few tests were made on them to show that they are very fine non-porous silicas without organic coating material on their surface.

Silica N showed cure-inhibiting properties at 10 volumes, and no cure was obtained at 20 volumes at either 300° or 400°F. curing. Syton SPR shows similar cure-inhibiting properties which are more pronounced at 400°F. It is probable that these silicas are too acidic and, therefore, exert a depolymerizing action on the polymer, in addition to catalyzing the decomposition of peroxide. The very low durometers obtained indicate also that their particle size is not sufficiently small for reinforcing properties.

Silica K-233F is of the Santocel type, but does not show an appreciable degree of reinforcement. The same is true of sample I-P-3.

5. <u>Burgess Iceberg Pigment.</u>

Burgess Iceberg pigment, a calcined aluminum silicate, was previously found to show moderate reinforcement with SE-76 at high volume loadings. There was indication that this pigment might have good high temperature properties, and additional tests were made to check this. Data in Table I-A-5 show that the durometer of a typical stock increased 18 points upon curing at 480°F., indicating that this pigment does not impart the expected high temperature stability.

B. <u>Treatment and Variation of Silicone Polymer.</u>

In our previous quarterly report it was noted that different

TABLE I-B-1

Pretreated SE-76 (11317-5) and Santocel C

Compound No.	Treatment of SE-76	Vol.%	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2228 (A)	None (Control)	15	1 hr. @ 300°F.	947	425	36	309	897
(B)			24 hrs. @ 300°F.	775	350	38	383	---
(C)			24 hrs. @ 400°F.	864	325	42	438	---
2263 (A)	Heated 3 hrs. @ 300°F.	15	1 hr. @ 300°F.	664	325	53	364	---
(B)	in air to 8.4% wt. loss		24 hrs. @ 400°F.	650	312	49	391	---
2269-1 (A)	Heated 16 hrs. @ 480°F.	15	1 hr. @ 300°F.	673	175	58	---	---
(B)	in air to 17.4% wt. loss		16 hrs. @ 400°F.	651	150	60	---	---

Footnotes:
(1) Gen. Elec. SE-76 gum used with 2.0% benzoyl peroxide as a curing agent.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

lots of SE-76 as received from the General Electric Company appeared to be of varying viscosities. We found by actual viscosity measure and molecular weight determination that this was the case, and that average molecular weights of the different batches of gum varied from 400,000 to 800,000. The batches produced more recently have the lower molecular weights.

In checking the effect of molecular weight on physical properties of typical stocks, we determined also the stability of each to high temperature curing. In addition, the presently available polymer was heat-treated before compounding.

1. Heating SE-76 Polymer.

One of the objectives in our compounding program is to improve the high temperature stability of silicone rubber stocks. We know that extensive curing at 400°F. or higher stiffens the compounds, and that some recipes are more susceptible to change than others. This is especially true of the GS Silica compounds, which become brittle at 400°F. or higher.

It is possible that this effect is due to volatilization of the low molecular weight fraction from the polymer. In order to check this idea , standard recipes were cured with SE-76 which had been preheated to remove this fraction of the polymer first.

Table I-B-1 shows that heating the new lower molecular weight SE-76 (Batch 11317) (molecular weight approximately 430,000) at 300°F. results in a loss of 8.5 percent of volatile material, while the loss is 17.5 percent at 480°F. Stocks made with Santocel C and a standard benzoyl peroxide cure, using the SE-76 as received showed a greater change in elongation modulus and hardness between

TABLE I-B-2

Pretreated SE-76 (11317-5) and GS199S Silica

Compound No.	Treatment of SE-76	Pigment	Vol.%	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2229 (A)	None (Control)	GS199S	25	1 hr. @ 300°F.	495	837	65	167	226
(B)				24 hrs. @ 300°F.	690	825	66	184	271
(C)				24 hrs. @ 400°F.	965	425	80	570	915
2264 (A)	Heated 3 hrs. @ 300°F.	GS199S	25	1 hr. @ 300°F.	235	862	52	76	98
(B)	in air to 8.4% wt. loss.			24 hrs. @ 300°F.	535	837	57	143	220
2269-2 (A)	Heated 16 hrs. @ 400°F.	GS199S	25	16 hrs. @ 400°F.	538	300	77	443	---
(B)	in air to 17.4% wt. loss.			1 hr. @ 480°F.	721	50	85	---	---
2294 (A)	Heated 8 hrs. @ 200°F.		15	24 hrs. @ 400°F.	328	175	62	360	---
(B)	in vacuum.			6 hrs. @ 480°F.		Brittle			

Footnotes:
(1) Gen. Elec. SE-76 gum used without a curing agent.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

the 1 hour at 300°F. and the 16 or 24 hours at 400°F. cures than the comparable stocks made with gum that had been preheated at 300°F. or 480°F. Better elongation and tensile and lower hardness are obtained with the original unheated gum but better stability is obtained with the heated gum. This indicates that the fraction of the polymer responsible for poor heat stability of conventional compounds may be removed by heating, and that it constitutes from 8 to 17 percent of the entire polymer.

Table I-B-2 is a similar experiment, using GS199S Silica as the reinforcing pigment and curing agent. It is evident here with compound numbers 2229 and 2264 that the SE-76 preheated at 300°F. to 8 percent weight loss is no more stable in the 300°F. curing range than the original polymer. Numbers 2269-2 and 2294, which were taken up to 480°F., show definitely that this treatment will not prevent brittleness of GS Silica stocks in this range. There is great instability due to the pigment itself when cures are carried out at 400°F. or 480°F.

2. SE-76 of Varying Molecular Weight Cured with Peroxide.

Because of the difference between various batches of SE-76 siloxane polymer, it was of interest to determine whether their average molecular weight varied greatly. This was done in a separate series of experiments, described in the note below:

(a) Note on Molecular Weight of Silicone Polymers

Molecular weights of the various batches of SE-76 polymer were determined from viscosity data of dilute solutions using the method used by Flory et al (1).

Dilute solutions of each polymer were made at several

(1) Flory, P.J. et al J.Am.Chem.Soc., 74, 3364 (1952)

concentrations in methyl ethyl ketone. Their viscosity was determined at 26°C., using a standard Ostwald viscometer, and values for MEK, 26°C were determined for infinite dilution by extrapolation.

These data were then applied to the Staudinger equation:

$$[\eta] = KM^a \qquad (1)$$

where M is the molecular weight, and K and a are constants for a given polymer - solvent system at one temperature.

In order to find the values of these constants, the data of Flory et al (1) were used. Flory determined the limiting viscosity, $[\eta]$ MEK, values for polydimethylsiloxane fractions of known osmometric molecular weights at 20° and 30°C. in methyl ethyl ketone. From a plot of eq.(1) in the form:

$$\log[\eta] = \log K + a \log M \qquad (2)$$

the constants K and a were determined for 20° and 30°C.

Flory's data for $[\eta]$ MEK at 20° and 30°C. were replotted using the Arhenius equation:

$$[\eta] = Ae^{-B/T} \qquad (3)$$

to obtain values of $[\eta]$ at 26°C. for the fractions of known osmometric molecular weight. A third plot of equation (2) was then made to give constants K and a at 26°C. Values of M from our data at 26°C. could then either be read off the plot or calculated with the 26° constants.

Values for the Staudinger equation constants for polydimethyl siloxane in methyl ethyl ketone are as follows:

(1) Flory, P.J. et al J.Am.Chem.Soc. 74, 3364 (1952)

TABLE I-B-2-a

Staudinger Equation Constants from Flory's Data

Temp.° C.	Kx10^3	log K	[illegible]
20°	0.80	-3.099	0.50
26°	0.66	-3.178	0.52
30°	0.55	-3.255	0.54

The average molecular weight of the various batches of SE-76 from the limiting viscosity at 26°C are given below:

TABLE I-B-2-b

Average Molecular Weights from Viscometric Data

Batch No.	[η] MEK 26°C	Molecular Weight
81339	0.820	840,000
B-5946	0.760	730,000
8826	0.750	710,000
BX-2600	0.632	512,000
B-7155	0.615	483,000
11317(as recd)	0.584	433,000
Fractionated sample		
11317(high fract)	0.715	643,000
11317(medium ")	0.568	408,000
11317(low ")	0.522	352,000

TABLE I-B-3

Various Batches of SE-76 and Santocel C

Compound No.	Batch No.	Mol.Wt.	Pigment	Vol.%	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%
2228-1 (A)	B-5946	730,000	Santocel C	15	1 hr. @ 300°F.	835	325	51	485
(B)					24 hrs.@ 300°F.	805	300	56	580
(C)					24 hrs.@ 400°F.	595	237	50	520
2237-2 (A)	81339	840,000	Santocel C	15	24 hrs.@ 300°F.	870	362	50	390
(B)					16 hrs.@ 400°F.	815	287	55	485
(C)					24 hrs.@ 400°F.	580	275	55	415
2401-1 (A)	7155	483,000	Santocel C	15	1 hr. @ 300°F.	891	287	51	590
(B)					24 hrs.@ 300°F.	708	200	56	668
(C)					24 hrs.@ 400°F.	650	200	51	650
2228 (A)	11317	433,000	Santocel C	15	1 hr. @ 300°F.	947	425	36	309
(B)					24 hrs.@ 300°F.	775	350	38	383
(C)					24 hrs.@ 400°F.	864	325	42	438

Footnotes:
(1) Gen. Elec. SE-76 gum (different batches) with 2.0% benzoyl peroxide as a curing agent.
(2) Press cure 15 minutes at 230°F., oven cure as indicated.

As given in Table I-B-3, the average molecular weight of various batches of SE-76 varied from 433,000 to 840,000. Batch number B-5946, with which most of our work in 1951 and early 1952 was carried out, had an average molecular weight of 730,000 while batch 11317 which was used during the latter part of 1952 has the lowest average molecular weight of 433,000. This is about 50 percent lower and is a deliberate change in the polymer to impart better plasticity or workability to silicone compounds.

There is no great variation in properties of a standard 15 volume Santocel C stock, cured with benzoyl peroxide, as the molecular weight of the gum is changed. Data are given in Table I-B-3. Elongation and low hardness appear to be preserved during high temperature cures in the lower molecular weight gum to a better degree than with the higher molecular weight gum as shown also in Table I-B-1 where higher molecular weight was obtained by distilling off the volatile low molecular weight fractions.

C. Press Curing Studies

1. Press Curing SE-450 Stock

In 1951 we reported the results of a press and oven curing study of SE-450 stock (formerly called General Electric 81223 stock). At that time it was found that the best tensile strength

TABLE I-C-1

Low Temperature Press Curing SE-450 Stock

Compound No.	Stock	Press Cure	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%	Comp. Set 70 hrs. @ 300°F.
2393 (A)	G.E. 81223	10 min.@200°F.	1 hr. @ 300°F.	584	225	45	560	---	82
(B)			24 hrs. @ 480°F.	594	250	41	486	---	63
2393-1 (A)	G.E. 81223	10 min.@210°F.	1 hr. @ 300°F.	833	275	44	525	---	80
(B)			24 hrs. @ 480°F.	777	262	41	---	---	63
2393-2 (A)	G.E. 81223	10 min.@220°F.	1 hr. @ 300°F.	430	200	46	430	---	83
(B)			24 hrs. @ 480°F.	592	212	45	540	---	68
2393-3 (A)	G.E. 81223	10 min.@230°F.	1 hr. @ 300°F.	825	287	46	500	---	86
(B)			24 hrs. @ 480°F.	655	237	44	550	---	71

Footnotes:
(1) Gen. Elec. SE-450 silicone rubber used (SE-76 with Santocel CS and 1.65% benzoyl peroxide as a curing agent).

TABLE I-C-2

Low Temperature Press Curing Titanox RANC Stock (40 Vols.)

Compound No.	Stock	Press Cure	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%	Comp. Set 70 hrs. @ 300°F.
2394 (A)	SE-76 + 40 vol. Titanox RANC, 2% Benzoyl Peroxide	10 min. @ 200°F.	1 hr. @ 300°F.	448	337	34	235	---	100
(B)			24 hrs. @ 480°F.	383	212	35	322	---	69
2394-1 (A)	Same	10 min. @ 210°F.	1 hr. @ 300°F.	481	425	32	214	---	100
(B)			24 hrs. @ 480°F.	352	250	33	264	---	72
2394-2 (A)	Same	10 min. @ 220°F.	1 hr. @ 300°F.	408	325	35	225	---	100
(B)			24 hrs. @ 480°F.	342	213	36	328	---	73
2394-3 (A)	Same	10 min. @ 230°F.	1 hr. @ 300°F.	427	337	33	232	---	100
(B)			24 hrs. @ 480°F.	408	250	35	300	---	72

Footnotes:

(1) Gen. Elec. SE-76 gum used, with 2.0% benzoyl peroxide as a curing agent.

was obtained with a press cure of 15 minutes at 230°F. Furthermore, it was observed that lower compression set was obtained with a low temperature press cure and a high temperature oven cure.

Press curing was recently extended to lower temperatures, between 200° and 230°F. to see whether an optimum in properties would occur in this range. Data are given in Table I-C-1 and indicate that optimum compression set is obtained with a press cure of 200°-210°F. and a 480°F. oven cure. The higher tensile strength of the 210° press cure would indicate this to be preferable from an overall standpoint.

2. Press Curing a Titanox Stock

A similar series of press cures were given to a 40 volume Titanox RANC stock. Data in Table I-C-2 show that here, as with SE-450, a low temperature press cure leads to lower compression set values. However, this stock is not as sensitive to variations in press curing as is the SE-450 compound. The improvement in compression set brought about by low temperature press curing may be ascribed to reduced depolymerization in the press caused by benzoic acid which has not had a chance to volatilize.

D. Pigment Preheating Studies

1. Preheating Micronex Carbon

It is well known that carbon blacks generally inhibit peroxide curing of silicone rubber when present in sufficient amount to exert a reinforcing action. This effect is minimized with the curing agent tertiary butyl perbenzoate, with which weak cures in the presence of carbon black may be made.

TABLE I-D-1

Preheating Micronex Carbon W-6 in SE-76

Compound No.	Vol.% Pigment	Wt.% Peroxide	Preheating	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2395	25	4.0 tertiary butyl perbenzoate	None	87	25	49	---	---
2395-1	"	"	1 hr. @ 450°F.	63	25	48	---	---
2395-2	"	"	16 hrs. @ 400°F.	250	137	52	---	---
2395-3	25	4.0 benzoyl peroxide	None	27	87	25	---	---
2395-4	"	"	1 hr. @ 450°F.	25	100	26	---	---
2395-5	"	"	16 hrs. @ 400°F.	61	162	28	---	---

Footnotes:
(1) Gen. Elec. SE-76 gum used; curing agent is indicated.
(2) Press cure 15 minutes at 230°F.; oven cure 16 hours 400°F.

This inhibition of curing is most probably due to a catalytic decomposition or adsorption of the peroxide on the highly active surface of the carbon black. This surface, in addition to adsorbing polar organic molecules, has a considerable amount of chemically bound oxygen in the form of carbonyl complexes which may be acidic. These may be removed in part by heating at elevated temperatures in the absence of air. The preheating technique consists of heating the milled pigment and gum before addition of peroxide and curing.

In order to see whether a carbon black so treated would show less poisoning effect on peroxide, the experiments in Table I-D-1 were made. Without preheating a moderate degree of cure was obtained with perbenzoate (H = 49) but the reinforcement was poor (T = 87). No cure was obtained with peroxide (H = 25, T = 27). Using Micronex preheated 16 hours at 400°F. and perbenzoate, a better cure (H = 52) and a surprising degree of reinforcement were obtained (T = 250). With peroxide the cure and reinforcement were proportionately higher after preheating, but still were not extensive. It thus appears that carbon black could be used as a reinforcing filler for silicone rubber, if given a pretreatment which would effectively deactivate or deacidify its surface. Benzoyl peroxide would still not be as effective as tertiary butyl perbenzoate.

2. <u>Preheating Fine Titanium Dioxide.</u>

Samples of ultra-fine titanium dioxide, obtained from the National Lead Company, showed peroxide cure-inhibiting properties

TABLE I-D-2

Preheating Fine Titanium Dioxide Batches
(Titanox MP-561-6)

Compound No.	Vol.% Pigment	Preheating	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.(3) 200%	St.(3) 400%
2404-1	10	None	70	87	40	---	---
		1 hr. @ 450°F.	69	62	41	---	---
2404-2	20	None	236	125	52	---	---
		1 hr. @ 450°F.	290	87	52	---	---
2404-3	30	None	435	112	61	---	---
		1 hr. @ 450°F.	543	100	62	---	---
2404-4	40	None	590	125	72	---	---
		1 hr. @ 450°F.	660	87	73	---	---
2404-5	50	None	610	125	79	---	---
		1 hr. @ 450°F.	680	75	81	---	---
2404-6	60	None	500	75	88	---	---
		1 hr. @ 450°F.	585	50	90	---	---

Footnotes:
(1) Gen. Elec. SE-76 silicone gum used, 4.0% benzoyl peroxide as a curing agent.
(2) Press cure 15 minutes at 230°F.; oven cure 24 hours at 400°F.

similar to those of carbon black. Preheating tests were made on one of the samples, MP-561-6, in an attempt to deactivate the filler before addition of peroxide and cure. Results of a 450°F. preheating are given in Table I-D-2 and show that this treatment had a slight improving effect on the cures at 20 to 60 volume loading.

II. REINFORCEMENT OF SILICONE RUBBER WITH GS199S SILICA.

A. Control Compounding and Oven Curing Data

A considerable amount of attention has been focused on compounding with DuPont GS199S Silica because of its unusual properties and promise for the reinforcement of silicone rubber.

In the last quarterly report, No. 12, the initial work with this pigment was reviewed. GS199S is a very finely divided porous silica, containing an organic constituent as a coating. This constituent is chemically bound and may be removed as n-butyl alcohol. The coating oxidizes in air and is thus removed between 200 and 400°F. This pigment will not only reinforce silicone rubber to a high degree, but will also impart cure to the compound, so that a strong slab may be formed from the gum and pigment alone. Under optimum conditions, compounds of up to 1900 p.s.i. tensile strength with 850 per cent elongation were produced. The mechanism of curing has not yet been determined but is assumed to be related to breakdown of the coating.

The major disadvantage of GS Silica compounds is that they become overcured rapidly when subjected to temperatures over 400°F. and slowly at temperatures between 300 and 400°F. Since silicone rubber compounds are generally expected to withstand temperatures up to 500°F., and as many of the specification tests are carried out above 300°F., one of the outstanding properties of silicone rubber is sacrificed when GS Silica is used in the compound. The maximum useful temperature of these compounds at present is about 300°F.

TABLE II-A-1

Press Curing GS Silica Compounds

Compound No.	Pigment	Vol.% Pig.	Wt.% Benzoyl Peroxide	Press Cure	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2378	GS Silica	25	2.0	(A) 10 min. @210°F.	1 hr. @300°F. 3 hrs. @480°F.	1020	500	74 89	364	715
				(B) 10 min. @230°F.	1 hr. @300°F. 3 hrs. @480°F.	1300	688	73 91	313	613
				(C) 10 min. @250°F.	1 hr. @300°F. 3 hrs. @480°F.	1320	713	73 90	321	580
2378-1	GS Silica	25	0.5	(A) 10 min. @210°F.	1 hr. @300°F. 3 hrs. @480°F.	795	800	60 83	175	260
				(B) 10 min. @230°F.	1 hr. @300°F. 3 hrs. @480°F.	510	825	60 86	130	200
				(C) 10 min. @250°F.	1 hr. @300°F. 3 hrs. @480°F.	520	888	60 88	130	180

Footnotes:
(1) Gen. Elec. SE-76 gum used.
(2) Press and oven cures as indicated.

TABLE II-A-2

Oven Curing Various GS Silica Compounds

Compound No.	Pigment	Vol.% Pig.	Wt.% Benzoyl Peroxide	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2265-1	GS Silica	15	0	12 hrs. @ 400°F.	278	512	44	155	226
				44 hrs. @ 400°F.	362	225	64	353	---
				16 hrs. @ 480°F.	348	50	70	---	---
2265-2	GS Silica	15	0.5	12 hrs. @ 400°F.	567	525	55	287	455
				44 hrs. @ 400°F.	454	208	67	430	---
				16 hrs. @ 480°F.	325	75	67	---	---
2265-3	GS Silica	15	1.0	12 hrs. @ 400°F.	678	475	63	353	592
				44 hrs. @ 400°F.	425	163	71	404	---
				16 hrs. @ 480°F.	314	63	68	---	---
2266-1	GS Silica	25	0	12 hrs. @ 400°F.	819	650	72	314	476
				44 hrs. @ 400°F.	494	50	85	---	---
				16 hrs. @ 480°F.	39	10	93	---	---
2266-2	GS Silica	25	0.5	12 hrs. @ 400°F.	897	525	81	477	772
				44 hrs. @ 400°F.	518	50	83	---	---
				16 hrs. @ 480°F.	149	10	92	---	---
2266-3	GS Silica	25	1.0	12 hrs. @ 400°F.	915	412	82	552	868
				44 hrs. @ 400°F.	530	25	88	---	---
				16 hrs. @ 480°F.	234	25	94	---	---

Footnotes:
(1) Gen. Elec. SE-76 silicone gum used (Batch No. 11317).
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

1. Press Curing Data

Variation of press curing temperature was carried out with 25 volume GS199S Silica stocks containing 0.5 and 2.0 percent benzoyl peroxide. Low molecular weight gum, batch 11317 was used. Data are given in Table II-A-1.. With 0.5 percent peroxide, reinforcement was lowered as the press curing temperature was raised. The same was true using 2 percent peroxide, as indicated by the modulus data. These data are similar to those of Table I-C-1 and I-C-2 and again suggest that peroxide decomposition products are operative in depolymerizing the SE-76 in the presence of GS199S Silica. The 210°F. press cured slabs had higher elongations and did not become quite as hard at 480°F. However, this improvement was not sufficient to keep the 480°F. cured slabs from becoming stiff and brittle and therefore unsatisfactory.

2. Oven Curing Data

Table II-A-2 gives data on 400 and 480°F. oven cures of 15 and 25 volume GS Silica stocks with varying benzoyl peroxide. The regularly available lower molecular weight SE-76 siloxane polymer (Batch No.11317) was used.

The purpose of this series of tests was to determine high temperature curing properties of the low molecular weight polymer with GS Silica plus peroxide. Fifteen volume stocks withstand 44 hours at 400°F. without becoming brittle. However, from the standpoint of tensile the 12 hour cures at 400°F. were superior.

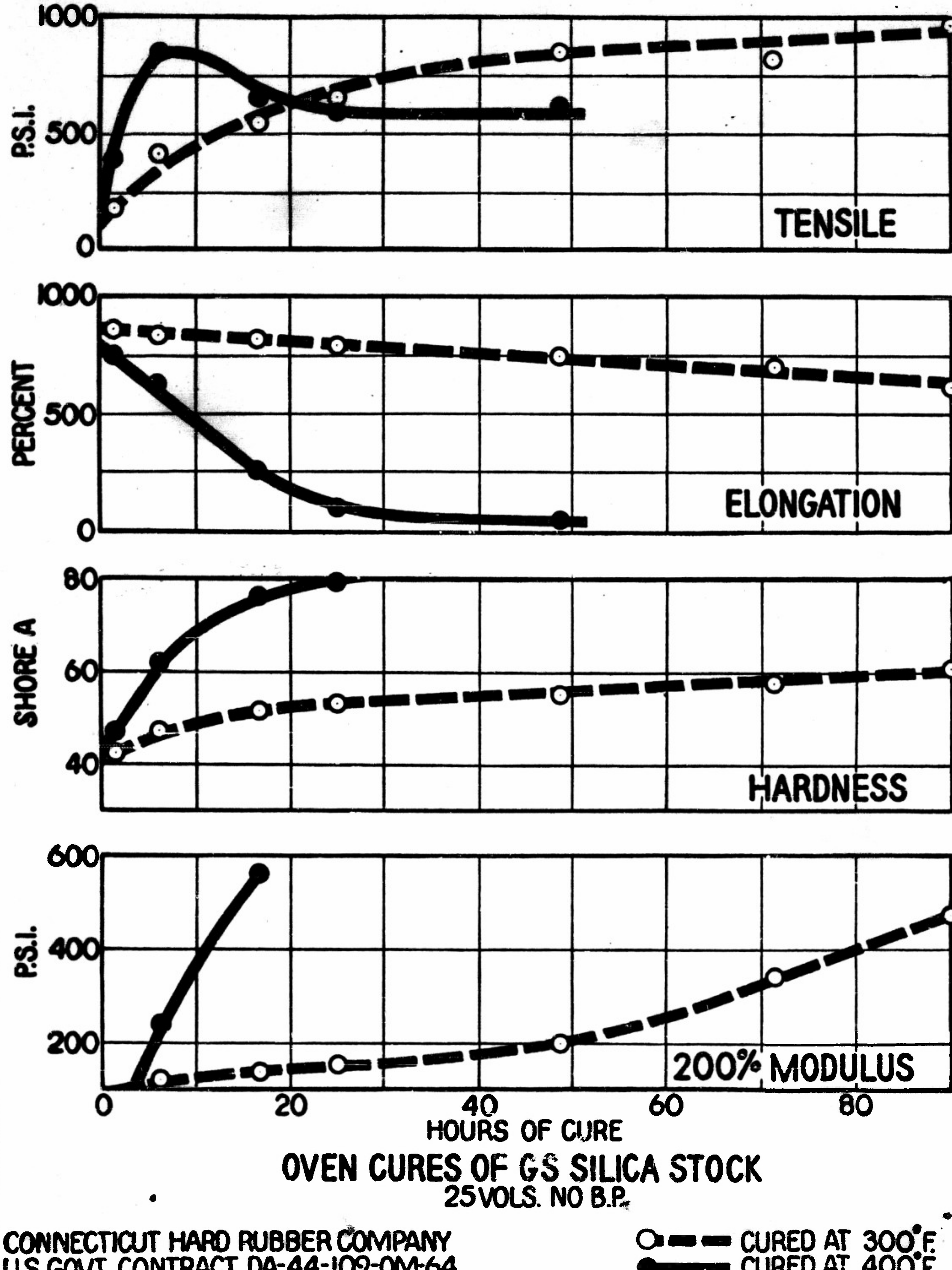
TABLE II-A-3

Oven Curing GS Silica Compounds

Compound No.	Pigment	Vol.% Pig.	Wt.% Benzoyl Peroxide	Oven Cure	Comp. Set (3)	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2344	GS Silica	25	0	(A) 1 hr. @ 300°F.	107	212	875	44	75	100
				(B) 6 " "	103	413	862	47	108	150
				(C) 16 " "	101	550	813	51	134	205
				(D) 24 " "	97	638	813	53	153	235
				(E) 48 " "	93	875	768	55	200	---
				(F) 72 " "	---	812	700	58	356	---
				(G) 96 " "	---	982	637	63	475	---
2344-1	GS Silica	25	0	(A) 1 hr. @ 400°F.	99	398	762	46	115	---
				(B) 6 " "	96	854	638	62	240	---
				(C) 16 " "	72	643	250	77	570	---
				(D) 24 " "	64	600	100	81	---	---
				(E) 48 " "	53	626	37	85	---	---
2344-2	GS Silica	25	0	(A) 1 hr. @ 450°F.	95	665	513	60	282	522
				(B) 6 " "	49	---	---	--	---	---
				(C) 16 " "	52	525	25	82	---	---
				(D) 24 " "	56	523	50	84	---	---
				(E) 48 " "	76	581	25	85	---	---
2344-3	GS Silica	25	0	(A) 1 Hr. @ 480°F.	---	491	125	74	---	---
				(B) 6 " "	---	445	25	85	---	---
				(C) 16 " "	---	Brittle		90	---	---
				(D) 24 " "	---	"		90	---	---
				(E) 48 " "	---	"		90	---	---

Footnotes:
(1) Gen. Elec. SE-76 silicone gum (Batch No. 11317) used.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.
(3) Percent of original deflection. By ASTM D395-49T (70 hours at 300°F.).

FIG. II-A-3



OVEN CURES OF GS SILICA STOCK
25 VOLS. NO B.P.

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA-44-109-QM-64

With 25 volumes of GS Silica, the 12-hour cure at 400°F. is the only satisfactory one, and all properties suffer with further curing. Other data show that with benzoyl peroxide present the highest elongation and tensile are obtained in short cures, 1 hour at 300 or 400°F., these properties falling off fairly rapidly with further curing. This is attributable to the effect of the pigment, the ultimate properties being independent of the concentration of benzoyl peroxide.

A further study of curing rate of GS Silica stocks is shown in Table II-A-3. This is a curing study of 25 volume GS 199S Silica compounds, with no benzoyl peroxide, using the available lower molecular weight gum (Batch No.11317). Curing temperatures were 300, 400, 450 and 480°F. with times from 1 to 96 hours. The data are represented graphically in Figure II-A-3 for 300 and 400°F. cures.

It is apparent that the reaction by which silicone rubber is cured with GS199S Silica is much slower than that with benzoyl peroxide, and the best stocks are obtained with a cure limited by time and temperature below the point where GS 199S Silica actively overcures. For highest strength an extended cure at 300°F. is indicated. A cure of 6 hours at 400°F. appears to be approximately equal to one of 50 hours at 300°F. Cures at 300°F. were not carried beyond 96 hours for practical reasons, but it appears that the tensile strength would continue to rise at a faster rate than elongation decreased for some time at this temperature. Evidence of further curing activity at 300°F.obtained from the compression set data obtained on tests run at this temperature. With 16 to 24 hours of curing at 400°F. or 6 hours at 450°F. the stocks have been sufficiently tightly cured that normal compression set values for typical benzoyl peroxide cured silicone stocks are obtained.(See Tables I-C-1 and I-C-2). It should be noted that the best compression sets occur only after the elongation has deteriorated badly and stiffness has increased greatly due to the extra cross-links set up.

3. Varying Molecular Weight Gum

The effect of polymer molecular weight of various batches of SE-76 on stocks cured with benzoyl peroxide was discussed previously (See Table I-B-3). It was found that there was no clear difference in reinforcement in the range of molecular weights from 400,000 to 800,000, and that properties varied more with curing temperature in the high molecular weight region. Overcuring is more likely with the high molecular weight gum.

With GS Silica reinforcement and cure, better tensile strength is obtained with higher molecular weight polymer. Data for these tests are given in Tables II-A-4, 5, and 6 in Figure II-A-6.

We found (Report No.12) that tensile strengths of over 1000 p.s.i. could not be obtained with Batch No.11317 gum, whereas strengths of almost 2000 p.s.i. had been obtained with

TABLE II-A-4

Fractionated SE-76 (11317-5) and 25 vols. GS199S

Compound No.	Batch No.	Mol.Wt.	Pigment	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
Average Values	11317-5(Control) (Not fractionated)	430,000	GS199S	1 hr. @ 300°F.	240	860	52	80	100
				24 " @ 300°F.	670	760	63	200	310
				24 " @ 400°F.	740	230	81	540	880
				16 " @ 480°F.	Brittle	< 25	88	---	---
2414-1	(A) Low Mol.Wt.	350,000	"	24 " @ 300°F.	707	600	65	256	440
	(B) Fraction			24 " @ 400°F.	495	50	81	---	---
2414-2	(A) Medium Mol.Wt.	410,000	"	24 " @ 300°F.	825	700	66	230	423
	(B) Fraction			24 " @ 400°F.	680	175	80	---	---
2414-3	(A) High Mol.Wt.	640,000	"	24 " @ 300°F.	1030	675	66	252	449
	(B) Fraction			24 " @ 400°F.	730	200	80	730	---

Footr. es:
(1) ·n.Elec. SE-76 gum used; fractionated as indicated. No benzoyl peroxide.
(2) -ess cure 15 minutes at 230°F.; oven cure as indicated.
(3)

TABLE II-A-5

Various Batches of SE-76 and 15 Vols. GS199S Silica

Compound No.	Batch No.	Mol.Wt.	Pigment	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
Average Values	B-5946	730,000	GS199S	24 hrs.@ 300°F.	1550	930	47	180	310
				16 " @ 400°F.	1360	740	59	290	520
				24 " @ 400°F.	1170	620	59	570	610
				6 " @ 480°F.	350	50	70	---	---
2372-1(A)	BX-2600	510,000	GS199S	1 " @ 300°F.	171	887	28	41	83
(B)				24 " @ 300°F.	465	825	38	100	176
(C)				16 " @ 400°F.	430	513	50	177	342
(D)				16 " @ 480°F.	229	37	75	---	---
Average Values	11317-5	430,000	GS199S	24 " @ 300°F.	390	810	44	110	200
				16 " @ 400°F.	390	520	50	210	280
				24 " @ 400°F.	390	200	61	---	---
				6 " @ 480°F.	380	90	69	---	---

Footnotes
(1) Gen.Elec. SE-76 gum used; various batches as indicated.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.
(3)

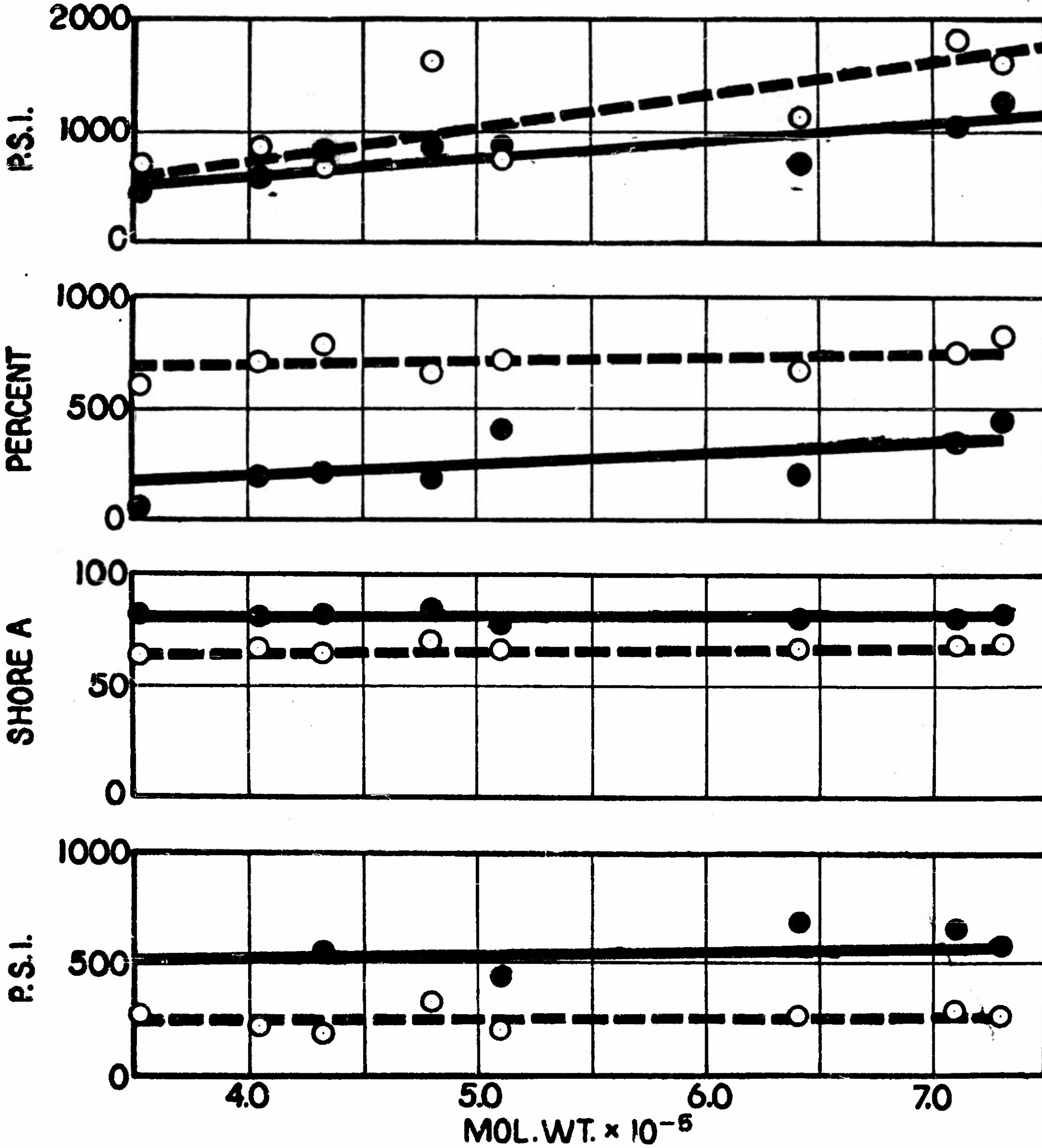
TABLE II-A-6

Various Batches of SE-76 and 25 Vols. GS199S Silica

Compound No.	Batch No.	Mol.Wt.	Pigment	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
Average Values	B-5946	730,000	GS199S	1 hr. @ 300°F.	1140	1030	57	140	210
				24 " @ 300°F.	1580	820	69	260	460
				16 " @ 400°F.	1320	500	80	540	970
				24 " @ 400°F.	1210	440	80	600	940
				6 " @ 480°F.	Brittle	<25	90	---	---
2372-2 (A)	BX-2600	510,000	GS199S	1 " @ 300°F.	286	825	52	92	137
(B)				24 " @ 300°F.	729	700	67	201	331
(C)				16 " @ 400°F.	765	400	77	450	765
(D)				1o " @ 480°F.	Brittle		94	---	---
2401-2 (A)	7155	480,000	GS199S	1 " @ 300°F.	1281	825	62	230	---
(B)				24 " @ 300°F.	1605	662	70	326	---
(C)				24 " @ 400°F.	765	162	86	---	---
(D)				16 " @ 480°F.	Brittle		88	---	---
2413-2 (A)	8826	710,000	GS199S	24 " @ 300°F.	1770	737	65	275	600
(B)				2.5 " @ 350°F.	1205	625	60	301	603
(C)				18 " @ 350°F.	1000	425	72	465	928
(D)				16 " @ 400°F.	1000	325	76	675	---
(E)				16 " @ 480°F.	141	25	90	Brittle	
Average Values	11317-5	430,000	GS199S	1 " @ 300°F.	240	860	52	80	100
				24 " @ 300°F.	670	760	63	200	310
				16 " @ 400°F.	790	420	78	460	640
				24 " @ 400°F.	740	230	81	540	880
				6 " @ 480°F.	Brittle	<25	88	---	---

Footnotes:
(1) Gen. Elec. SE-76 gum used; various batches as indicated.
(2)
(3) Press cure 15 minutes at 230°F.; oven cure as indicated.

FIG. II-A-6



GS SILICA IN SE-76 OF VARYING MOLECULAR WT.

25 VOLS. NO B.P.

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA-44-109-QM-64

CURED @ 300°F.
CURED @ 400°F.

Batch No.5946. This was traced to the difference in average molecular weight and led to evaluation of GS 199S Silica curing from this standpoint.

Table II-A-4 gives data on a batch of the 11317 gum which was separated by solvent precipitation into three different molecular weight fractions, which averaged 350,000, 410,000 and 640,000. Cures on the fractions show the highest tensile on the highest molecular weight fraction with little effect on other physical properties except that the highest fraction was also more stable at the 400°F. curing temperature.

Tables II-A-5 and II-A-6 contain data for a series of cures with 15 and 25 volumes of GS Silica in five different batches of SE-76. These batches were used as received, and their average molecular weight determined by the viscosity method as previously described (page 9a). Average molecular weights ranged from 430,000 for Batch No.11317 to 730,000 for Batch No.B-5946,

With 15 volumes of GS Silica (Table II-A-5, the best reinforcement occurred with Batch No.B-5946 of 730,000 molecular weight.

All of the available batches of SE-76 were compounded with 25 volumes of GS 19^S Silica, the data being given in Table II-A-6 and Figure II-A-6. There are several interesting points evident from inspection of the data and graph. There is a definite increase in tensile strength as molecular weight increases, i.e., from 200 - 800 p.s.i. at 430,000 molecular weight to 1000 - 1750 p.s.i. at 700,000 molecular weight. This occurs with either a 300° or 400°F. cure, although the result is more easily detected at the lower temperature of cure. This accounts for the failure to produce high tensile GS 199S Silica stocks with the regularly available low molecular weight variety of SE-76. Figure II-A-6 shows that as gum molecular weight increases, the tensile strength plot shows the biggest increase with a slight effect observable in elongation improvement. Other properties are not changed appreciably.

These data show that SE-76 rubber, to be most effective in compounding with GS Silica, should be of about 700,000 average molecular weight or more. This grade of polymer shows better tensile strength than the presently favored, lower viscosity type currently sold by the General Electric Company. It is recognized that softer, lower molecular weight gum is easier to mill and easier to "freshen" by milling after having been mixed and aged.

TABLE II-B-1

Compounds with Special GS199S Silicas

Compound No.		Pigment	Vol.% Pig.	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.@ 200%	St.@ 400%
2311	(A)	GS199S	15	24 hrs. @ 300°F.	420	900	43	98	---
	(B)	(3rd shipment)		24 hrs. @ 400°F.	384	125	65	---	---
	(C)	(Control)		6 hrs. to 480°F.	400	87	68	---	---
	(D)			24 hrs. @ 480°F.	184	50	78	---	---
2298	(A)	GS-2399-147	10	24 hrs. @ 300°F.	112	162	46	---	---
	(B)	(No coating)		24 hrs. @ 400°F.	49	<25	40	---	---
	(C)			6 hrs. to 480°F.	---	<25	46	---	---
	(D)			24 hrs. @ 480°F.	---	<25	40	---	---
2300	(A)	GS-2399-55B	15	24 hrs. @ 300°F.	390	25	80	---	---
	(B)	(One-half		24 hrs. @ 400°F.	---	<25	82	---	---
	(C)	coating)		6 hrs. to 480°F.	---	---	84	---	---
	(D)			24 hrs. @ 480°F.	---	---	--	---	---
2299	(A)	GS-2399-92C	15	24 hrs. @ 300°F.	230	600	32	---	---
	(B)	(Full coating)		24 hrs. @ 400°F.	130	175	55	---	---
	(C)			6 hrs. @ 480°F.	370	125	63	---	---
	(D)			24 hrs. @ 480°F.	---	<25	71	---	---
2301	(A)	GS-2399-56	15	24 hrs. @ 300°F.	28	150	25	---	---
	(B)	(Full coating.		24 hrs. @ 400°F.	27	50	22	---	---
	(C)	Larger part.		6 hrs. to 480°F.	27	62	20	---	---
	(D)	size.)		24 hrs. @ 480°F.	Depolymerized		12	---	---

Footnotes:
(1) Gen. Elec. SE-76 gum used; no curing agent.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

B. Special Types of GS Silica.

At our request the DuPont Company supplied other GS Silica samples which had varying amounts of the organic coating. Also, a sample of larger particle size was included for evaluation.

The question had naturally arisen as to whether GS Silica with less coating would effect a good cure, and if this were the case, whether less coating would prevent overcuring at temperatures above 400°F.

Table II-B-1 gives physical properties of compounds made with these pigments in SE-76 gum at cures of 300°, 400° and 480°F. Fifteen volume loadings were used except with GS-2399-147 which could not be milled higher than 10 volume per cent. In this experiment the control with regular GS199S Silica yielded a maximum of 420 p.s.i. tensile strength after a cure of 24 hours at 300°F. After 24 hours at 400°F., elongation was reduced to 125 per cent but the stock withstood 6 hours curing at 480°F. GS-2399-147, of the same particle size but with no coating, showed slight reinforcement at 10 volume loading. The pigment surface was so active that more than 10 volumes could not be added. This degree of reinforcement is similar to that obtained with Santocel C with no curing agent; hence the conclusion is that no cure was exhibited by this sample of GS Silica. The stock maintained its hardness at higher temperature cures, but the elongation dropped below 25 per cent. With sample GS-2399-55B, having one-half the usual organic coating, a tensile strength of 390 p.s.i. was developed with a 300°F. cure; however, the elongation was only 25 per cent. The high durometer of this cure indicates that the optimum volume loading was probably exceeded. Sample GS-2399-82C had a full coating, but developed only 230 p.s.i. tensile strength, considerably lower than that of the standard GS199S. This is probably due to a slight difference in particle size. The sample which definitely had a larger particle size and a full coating gave practically no reinforcement, showing again the importance of proper pigment size. The other noteworthy point with this compound was the fact that it becomes softer rather than harder as the curing temperature was raised.

These compounds lend valuable information with regard to the curing and stiffening action of GS Silica. With no organic coating, only 10 volumes could be milled into SE-76 with slight reinforcement, and the stock did not become stiff as curing temperature increased. With one-half coating, 15 volumes could be introduced to produce a very short, high durometer stock which became stiffer at higher temperature cures. With a full coating on the pigment and small particle size, good reinforcement with high elongation was obtained with 300°F. cures. These became about as stiff as the one-half coated pigment at 400 and 480°F. Finally, the fully coated large particle size GS stock at the same volume loading showed no reinforcement or cure and became softer as the curing temperature increased.

From our work on the pigment alone, we know that the organic coating on GS Silica breaks down and comes off easily above 400°F. when heated in air. This evidently occurs to some degree in the

TABLE II-B-2

Compounds with Uncoated GS Silicas

Compound No.	Pigment	Vol.% Pig.	Wt.% Benzoyl Peroxide	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St.* 200%	St.* 400%
2354 (A)	GS-2399-147 (No coating)	5	2.0	16 hrs. @ 400°F.	224	337	28	140	---
(B)				16 hrs. @ 480°F.	232	350	47	130	---
2354-1 (A)	Same	10	2.0	16 hrs. @ 400°F.	225	150	51	---	---
(B)				16 hrs. @ 480°F.	149	175	47	---	---
2355 (A)	GS199S (Coating removed by heating.)	5	2.0	16 hrs. @ 400°F.	210	413	25	92	---
(B)				16 hrs. @ 480°F.	224	450	22	75	---
2355-1 (A)	Same	10	2.0	16 hrs. @ 400°F.	425	175	50	---	---
(B)				16 hrs. @ 480°F.	145	225	43	150	---
2356 (A)	Same +5% Ultrawet	11.6	2.0	16 hrs. @ 400°F.	392	325	66	266	---
2251	Santocel C	10	2.0	1 hr. @ 300°F.	614	463	45	---	---

Footnotes:
(1) Gen. Elec. SE-76 gum used, with benzoyl peroxide as curing agent.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

same manner when the pigment is dispersed in SE-76, so that the coating is partially removed in the 400°F. cure and to a much greater extent in the 480°F. cure. Stiffening of the stock is not, however, caused by a chemical action of the coating or its decomposition products on the gum since the fully coated large particle size sample did not show this effect. The GS Silica apparently becomes highly absorptive when the coating is removed from its surface. If the amount of absorptive surface is high (i.e. if the particle size of the pigment is small), the polymer becomes so extensively bound to the pigment that the resulting system is not flexible.

It was of interest to compare the reinforcing action of GS Silicas without coatings, with that of a silica such as Santocel C, using a benzoyl peroxide cure. Table II-B-2 gives results with GS-2399-147, supplied without coating, and with regular GS199S whose coating was completely removed by heating to 600°F. These samples could be milled to 10 volume loading only, and it is evident that reinforcemt is not great at this concentration compared with Santocel C. We have found by electron microscope observation that GS Silica and Santocel C have about the same ultimate particle size. The difference in reinforcement observed here may be due to a difference in porosity of the two silicas.

It was evident that the large particle size GS sample could not be milled at higher concentrations than GS199S. Properties of compounds up to 47 volume per cent loading are given in Table II-B-3. Optimum reinforcement is obtained at 20 volume per cent;

TABLE II-B-3

Compounds with GS-2399-56 (Large Particle Size)

Compound No.	Pigment	Vol.% Pig.	Wt.% Benzoyl Peroxide	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	St. @ 200%	St. @ 400%
2347	GS-2399-56	20	2.0	24 hrs. @ 300°F.	326	150	61	---	---
2347-1		"	None	" " "	125	150	50	---	---
2348		40	2.0	24 hrs. @ 300°F.	Brittle		95	---	---
2348-1		"	None	" " "	115	<25	91	---	---
2349		46.6	None	24 hrs. @ 300°F.	Brittle				

Footnotes:
(1) Gen. Elec. SE-76 gum used, curing agent benzoyl peroxide.
(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

above this the pigment loading is too high. If this pigment were similar to GS199S, and of larger particle size, one would expect its reinforcing action to approach that of GS199S at the proper loading.

TABLE II-C-1

COMPOUNDS WITH DRIED GS SILICA

Compound No.	Pigment	Volume % Pigment	Oven Cure	T	E	H	Stress @ 200%	Stress @ 400%
2311 (A)	GS-199S	15	24 hrs. 300°F.	420	900	43	98	
(B)	(control)		16 hrs. 400°F.	384	125	65	--	
(C)			6 hrs. 480°F.	400	87	68	--	
(A)	GS-199S	15	24 hrs. 300°F.	440	750	49	113	195
(B)	dried over $Mg(ClO_4)_2$		16 hrs. 400°F.	408	475	55	216	363
(C)	in vacuum		6 hrs. 480°F.	331	125	65		

(1) General Electric SE-76 silicone gum (11317) used, no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cures as indicated.

TABLE II-C-2

COMPOUNDS WITH GS-199S SILICA HEATED IN AIR

Compound No.	Pigment & Treatment	Volume % Pigment	Oven Cure	T	E	H
2311 (A)	GS-199S (control)	15	24 hrs. 400°F.	384	125	65
(B)			24 hrs. 480°F.	184	50	78
2279 (A)	GS-199S. Heated @ 300°F. in air	15	24 hrs. 400°F.	116	50	50
(B)	to 3.0% weight loss.		16 hrs. 480°F.	Brittle		82
2279-1 (A)	GS-199S. Heated @ 400°F. in air	15	24 hrs. 400°F.	Brittle		84
(B)	to 11.3% weight loss.		16 hrs. 480°F.	Brittle		--
2279-2 (A)	GS-199S. Heated @ 480°F. in air	10	24 hrs. 400°F.	48	88	32
(B)	to 16.5% weight loss.		16 hrs. 480°F.	74	175	30

(1) General Electric SE-76 silicone gum used, no curing agent.

(2) Press cure 15 min. 230°F.; oven cures as indicated.

TABLE II-C-3

COMPOUNDS WITH GS-199S SILICA HEATED IN VACUUM

Compound No.		Pigment & Treatment	Volume % Pigment	Oven Cure	T	E	H	Stress @ 200%
2412	(A)	GS-199S (control)	15	24 hrs. 300°F.	370	712	45	126
	(B)			16 hrs. 400°F.	379	362	56	266
	(C)			6 hrs. 480°F.	400	87	68	---
	(D)			16 hrs. 480°F.	235	25	71	---
2411	(A)	GS-199S. Heated to 480°F. in vacuum to 4.1% weight loss.	15	24 hrs. 300°F.	487	712	54	153
	(B)			16 hrs. 400°F.	459	362	64	306
	(C)			16 hrs. 480°F.	220	25	73	---
2351	(A)	GS-199S. Heated to 480°F. in vacuum to 4.1% weight loss.	15	24 hrs. 300°F.	560	675	60	195
	(B)			16 hrs. 400°F.	476	375	64	312
	(C)			6 hrs. 480°F.	312	100	72	

(1) General Electric SE-76 silicone gum used, no curing agent.

(2) Press cure 15 min. 230°F.; oven cures as indicated.

C. Treatment of GS-199S Silica

It has been noted that surface moisture on pigments has in some cases a considerable effect on reinforcement. In general, we have found that bone dry pigments are more effective, and pigment efficiency increases as it is dried by heating, up to the point where a chemical change or sintering takes place. GS-199S is markedly hydrophobic to liquid water; however, it can probably pick up a thin layer of vapor from the air. To check this, GS-199S Silica was dried over $Mg(ClO_4)_2$, with a resulting 1 per cent weight loss.

Data in Table II-C-1 show that this amount of moisture greatly affected the reinforcing or curing properties of the pigment. One difference is that the dried GS-199S stock does not become stiff as rapidly at 400°F. or 480°F. This would indicate an enhancing effect of moisture on the rate of the GS-199S Silica curing reaction.

Further compounds were made with GS-199S from which part or all of the coating had been removed by heating in air. Data in Table II-C-2 on compounds made with GS-199S heated in air show that after heating at 300°F. with a 3 per cent weight loss, GS-199S lost much of its reinforcing and curing action. This was completely destroyed by further heating at 400°F and 480°F.

Table II-C-3 gives data for GS-199S which was heated in vacuum at 480°F. to a 4 per cent weight loss. In

TABLE II-D-1

HIGH TEMPERATURE CURING OF GS SILICA STOCKS

Compound No.	Pigment	Volume % Pigment	Oven Cure	T	E	H	Stress @ 200%
2261 (A)	GS Silica	10	1 hr. 480°F.	199	350	35	143
(B)			4 " "	158	163	45	---
(C)			8 " "	176	138	43	---
(D)			8 " "	170	163	43	---
(E)			16 " "	131	113	43	---
2262 (A)	GS Silica	15	1 hr. 480°F.	400	300	57	364
(B)			4 " "	351	100	69	---
(C)			8 " "	339	83	71	---
(D)			8 " "	344	75	70	---
(E)			16 " "	291	50	72	---

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cures as indicated.

this case, reinforcing and curing properties were slightly enhanced by the heating. A difference between heating to similar weight losses, in air and in vacuum, is evident. The organic coating on GS-199S is apparently easily oxidized at 300-480°F. in air; thus, heating in air probably causes a considerable destruction of the original form of the coating with a measurable weight reduction, resulting in loss of curing properties. Heating in vacuum prevents this oxidation and a one-third loss of the coating does not affect curing properties greatly. The coating is evidently very firmly bound to the silica, probably by chemical bonds. Yet even the heated pigment continues to possess curing activity at 400 and 480°F.

D. High Temperature Compounding and Curing of GS Silica Stocks.

The major deficiency in high tensile strength silicone rubber as compounded with GS-199S Silica is its poor heat resistance. A stock containing 15 or 25 volumes of GS-199S Silica will cure well at 300°F., and maintain its properties at this temperature up to 100 hours plus. However, at 400°F. the stock will gradually become harder, while at the usual 480°F. curing temperature for silicone rubbers it will rapidly become brittle.

Table II-D-1 gives data on the stability of 10 and 15 volume GS stocks at 480°F. Obviously, reduced crosslinking should occur with a 10 volume loading. However, at a 10 volume loading, reinforcement is initially too low to be practical, and a good stock is not obtained with 300°F. curing. It was considered possible, due to the nature of the GS Silica curing action, that a low volume stock such as this might produce a good cure at higher temperatures. However, this was found not to be the case. Tensile strength and elongation both decrease with greater than one hour at 480°F. The stock retained 100 percent elongation after 16 hours, however, so it did not become brittle as do more highly loaded compounds. The initial tensile and elongation were not high enough indicating lack of reinforcement. With fifteen volumes of GS-199S, an initial elongation of 300 percent is reduced to 50 percent after 16 hours at 480°F., which places the stock in an almost brittle condition. A 25 volume stock becomes brittle after about 6 hours at this temperature.

1. Remilling GS Silica Stocks

It is well known that silicone stocks containing silica pigments such as Santocel-C need to be remilled after aging 24 hours in order to obtain optimum reinforcement. This is presumably due to the fact that the silicone polymer requires considerable time to be absorbed into the porous silica structure. When this process has been

TABLE II-D-2

REMILLING GS SILICA STOCKS

Compound No.	Pigment	Treatment	Volume % Pigment	Oven Cure	T	E	H	Stress @ 200%	Stress @ 400%
2284	GS Silica	Control	15	24 hrs. 400°F.	380	117	58	---	---
		Remilled (3)	"	+ 9 hrs. 480°F.	440	400	55	254	440
2285	"	Control	25	24 hrs. 400°F.	583	88	83	---	---
		Remilled (3)	"	+ 9 hrs. 480°F.	798	375	75	508	---
2286	"	Control	30	24 hrs. 400°F.	150	0	93	---	---
		Remilled (3)	"	+ 9 hrs. 480°F.	734	150	89	---	---
2287	"	Control	35	24 hrs. 400°F.	135	0	95	---	---
		Remilled (3)	"	+ 9 hrs. 480°F.	731	63	93	---	---

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cure as indicated.

(3) Compounds were remilled each day for 3 days before curing.

TABLE II-D-3

REMILLING GS SILICA STOCKS AFTER HEATING

Compound No.	Pigment		Volume % Pigment	Oven Cure	T	E	H	Stress @ 200%
2270-1(A)	GS Silica	Not remilled	25	3 hrs. 480°F.	565	100	80	--
(B)			"	12 " "	451	25	89	--
2270-2(A)	"	Remilled 30 min.	"	3 hrs. 480°F.	695	275	75	610
(B)			"	12 " "	613	75	84	--
2270-3(A)	"	Heated 200°F. 16 hrs.	"	3 hrs. 480°F.	610	200	76	610
(B)		& remilled 30 min.	"	12 " "	538	50	83	--
2272-1(A)	GS Silica	Not remilled	35	3 hrs. 480°F.	264	25	93	
(B)				12 " "	350	25	95	
2272-2(A)	"	Heated 200°F. 16 hrs.	"	3 hrs. 480°F.	675	50	90	
(B)		& remilled 30 min.	"	12 " "	550	25	94	

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cure as indicated.

completed, a rather inflexible network is formed and the compounded rubber will not flow in a press. Remilling softens the structure without destroying the effectiveness of the polymer-pigment bonds. It was postulated that the high temperature stiffening properties of GS Silica compounds might be lessened by such remilling, if this stiffening were due to polymer absorption on the pigment during curing.

Table II-D-2 gives data on remilled GS 199S Silica stocks of 15 to 35 volume loading. In all cases this repeated remilling before curing lowered the durometer, increased the elongation, and markedly increased the tensile strength of these compounds when cured at 480°F. The 480°F. cure of 9 hours given to these stocks is only a partial cure; however the results are sufficiently improved to indicate that this type of remilling would stabilize GS 199S stocks up to 25 volumes to withstand a 24 hour cure at 480°F.

Further remilling experiments were done to study this effect further. Data in Table II-D-3 show that 30-minute remilling, 24 to 48 hours after compounding, definitely improves a 25 volume GS stock in short cures at 480°F. It was thought that a preheating of the GS stock at some temperature below the 300°F. curing temperature might be advantageous. Compound 2270-3 was remilled 30 minutes after being heated 16 hours

TABLE II-L-4

SPECIAL TECHNIQUES WITH GS SILICA STOCKS

Compound No.	Pigment	Volume % Pigment	Compounding Data	Cure	T	E	H	Stress @ 200%
2317 (A)	GS Silica	25	Short milling - no refining. 15 min. press.	16 hrs. 400°F.	714	338	83	
(B)				6 hrs. 480°F.	470	[illegible]	92	
2342-1	GS Silica	25	Remilled, 5 min. press, removed cold	16 hrs. 400°F.	798	452	70	405
2342-2	"	"	Not remilled, 5 min. press, removed cold	16 hrs. 400°F.	860	475	66	420
2342-3	"	"	Remilled, 5 min. press, removed hot.	16 hrs. 400°F.	823	430	70	395
2342-4	"	"	Not remilled, 5 min. press, removed hot.	16 hrs. 400°F.	570	225	73	500

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cure as indicated at 230°F.; oven cure as indicated.

at 200°F., with some improvement in temperature stability. The same treatment of a 35 volume stock, #2272-2, showed a large increase in tensile strength. Prolonged (12 hours) curing at 480°F. overcame the improvement imparted by remilling.

It is concluded from these tests that one or two remilling treatments are beneficial to GS Silica stocks from all standpoints, and especially with regard to their resistance toward brittleness at 480°F.

2. <u>Curing Techniques with GS Silica Stocks</u>

With benzoyl peroxide cured silicone stocks, curing is carried out in two stages. The first is a press cure, in which the stock is molded under pressure and heat. This is usually done for 15 minutes at 230-250°F., which is sufficient to set the shape and complete the peroxide curing reaction. Because the decomposition products of the peroxide (i.e. benzoic acid) are harmful, the remainder of the curing up to 480°F. is carried out in an air circulating oven where this and other volatile products are removed from the stock. Since no peroxide is involved in the GS Silica curing mechanism, it was of interest to try other curing techniques.

Table II-D-4 gives data on short pressing times for a standard 25 volume GS stock. Since the GS Silica curing action is much slower than that of peroxide,

TABLE II-D-5

CURING GS SILICA STOCKS IN MOLD

Compound No.	Pigment	Volume % Pigment	Weight % B.P.	Curing Data	T	E	H	Stress 200%
2313-1(A)	GS Silica	25	None	Press: 15 min. 230°F. Oven: 16 hrs. @ 400°F. in mold	Brittle		76	
2313-1(B)	"	"	"	Press: 1 hr. @ 400°F. Oven: 16 hrs. @ 400°F. in air	217	250	74	217
2313-1(C)	"	"	"	Press: 1 hr. @ 400°F Oven: 16 hrs. @ 400°F. in mold	Brittle		81	
2313-2(A)	Santocel C	15	2.0	Press: 15 min. @ 230°F. in mold Oven: 16 hrs. @ 400°F.	No cure, soft			
2313-2(B)	"	"	"	Press: 1 hr. @ 400°F. Oven: 16 hrs. @ 400°F. in air	117	363	19	60

(1) General Electric SE-76 silicone gum used; benzoyl peroxide as curing agent.

(2) Press and oven cures as indicated.

very little, actual curing takes place during a standard 15 minute press cure at 230-250°F., this step being useful mainly to mold the stock. Slabs were therefore given very short times in the press, removed both hot and cold, and cured 16 hours at 400°F. in an air oven. In addition, the stocks were remilled once before molding. Results indicate that an orthodox press cure is unnecessary with GS stocks, that they may be removed either hot or cold from the mold, and the cure carried out in the oven entirely.

It was also of interest to determine the effect of extended mold cures, and higher temperature press cures on GS stocks. Data for this type of curing with both a standard 25 volume GS stock and a 15 volume Santocel-C, 2 percent benzoyl peroxide stock are given in Table II-D-5. The necessity for air oven curing with benzoyl peroxide is evident with compound number 2313-2(A) in which the 400°F. heating within an enclosed mold resulted in depolymerization of the rubber and no cure. Likewise, a long cure in the press at 400°F. caused partial depolymerization of this stock, and a resulting hardness of only 19.

The GS silica stock likewise did not survive extended heating in a mold, but became very brittle instead of soft as was the case with the peroxide stock. The result was a definite overcure by the GS silica. The

TABLE II-D-6

VARYING PEROXIDE AND PRESS CURE OF GS SILICA STOCKS

Compound No.	Pigment	Press Cure	Volume % Pigment	Weight % B.P.	Oven Cure	T	E	H	Stress @ 200%
2403-1(A)	GS Silica	10 min. @ 210°F.	25	3.0	1 hr. 300°F.	695	225	76	650
(B)	"		"	"	16 hrs. 400°F.	Brittle		81	---
(C)	"		"	"	16 hrs. 480°F.	Brittle		84	---
2403-2(A)	GS Silica	10 min. @ 300°F.	25	3.0	1 hr. 300°F.	957	237	70	890
(B)	"		"	"	16 hrs. 400°F.	Brittle		86	---
(C)	"		"	"	16 hrs. 480°F.	Brittle		92	---
2403-3(A)	GS Silica	10 min. @ 210°F.	25	0.5	1 hr. 300°F.	740	650	73	240
(B)	"		"	"	16 hrs. 400°F.	670	25	83	---
(C)	"		"	"	16 hrs. 480°F.	Brittle		76	---
2403-4(A)	GS Silica	10 min. @ 300°F.	25	0.5	1 hr. 300°F.	670	712	65	190
(B)	"		"	"	16 hrs. 400°F.	562	37	83	-
(C)	"		"	"	16 hrs. 480°F.	Brittle		86	-

(1) General Electric SE-76 silicone gum used; benzoyl peroxide as curing agent.

(2) Press and oven cures as indicated.

reason for this is not known, but it is evident that the proper procedure for GS silica curing is an air oven cure following short molding.

It has been shown previously (Section II-A-3) that silicone gum of a higher molecular weight polymer is much more responsive to GS silica curing. It was postulated that the lower physical properties obtained with the present SE-76 are due to the presence of too much low molecular weight polymer. Heating the gum to drive this off before compounding did not prove successful. However, it might be possible to cure partially, or cross-link this low molecular weight material with peroxide before the GS silica cure begins. This idea was tried, and the results are recorded in Table II-D-6.

With a short oven cure at 300°F., the highest tensile GS silica stock is obtained with 3.0 percent benzoyl peroxide and a 300°F. press cure. For higher temperature cures, the 0.5 percent peroxide stock is more satisfactory. None of the compounds has improved temperature resistance. The benzoyl peroxide effects a more rapid cure of the stock in the 250-300°F. range, and this is not impeded by the presence of GS silica. However, this initial cross-linking still does not bring the low molecular weight SE-76 into the class of the higher molecular weight material

TABLE II-D-7

PLASTICIZING GS SILICA STOCKS WITH SILICONE OILS

Compound No.	Pigment	Volume % Pigment	Plasticizer & Milling	Oven Cure	T	E	H	Stress @ 200%
2315-1(A)	GS Silica	25	Control - none	16 hrs. 400°F.	560	112	84	--
				6 hrs. 480°F.	603	37	90	--
2315-2(A)	"	"	5% #1000 silicone oil	16 hrs. 400°F.	505	25	86	--
(B)			added to gum	6 hrs. 480°F.	430	25	91	--
2315-3(A)	"	"	10% same	16 hrs. 400°F.	510	62	86	--
(B)				6 hrs. 480°F.	550	37	89	--
2321-1(A)	GS Silica	15	Control	16 hrs. 400°F.	275	50	70	--
(B)				6 hrs. 480°F.	122	25	73	--
2321-2(A)	"	"	5% #1000 silicone oil	16 hrs. 400°F.	297	50	70	--
(B)			added to gum	6 hrs. 480°F.	238	25	71	--
2321-3(A)	"	"	10% same	16 hrs. 400°F.	235	38	69	--
(B)				6 hrs. 480°F.	134	25	69	--
2321-4(A)	"	"	20% same	16 hrs. 400°F.	210	25	72	
(B)				6 hrs. 480°F.	Brittle		73	--

(1) General Electric SE-76 silicone gum used, no curing agent.

(2) Press cure 15 min. at 230°F.; oven cures as indicated.

for GS silica curing.

3. Plasticizing GS 199S Silica Stocks

Another series of experiments were carried out to test the utility of plasticizing GS silica-silicone rubber stocks so that they would be flexible after a full cure at 450-500°F. It is possible to soften silicone stocks to practically any degree with compatible plasticizers, and some of these will remain in the stock at the elevated temperatures desired here.

Data in Table II-D-7 give results using G.E. 9996-1000 silicone oil as a plasticizer. This is a "stopped" oil of high viscosity, and is not appreciably volatile at 450°F. Five and 10 percent of this oil failed to plasticize a 25 volume GS silica stock cured either at 400°F. or 480°F. The stocks are actually cured harder than they would if the oil were not present. The test was carried further using up to 20 percent silicone oil in a 15 volume GS stock. Durometer is higher with the oil-containing compounds in this case also. This result seems to tie in with the observation that harder gum (higher molecular weight) stands curing at 400°F. better than softer gum.

Another silicone oil known as G-2 was tried as a plasticizer because of its chemical properties. This oil was produced in our laboratory by acid depolymerization of GE9997-G silicone gum and

TABLE II-D-8

PLASTICIZING GS SILICA STOCKS WITH G-2 OIL

Compound No.	Pigment	Volume % Pigment	Compounding Procedure	Oven Cure	T	E	H	Stress @ 200%
2327-1(A)	GS Silica	15	Control	16 hrs. 400°F.	480	500	56	240
(B)				(A) + 6 hrs. 480°F.	410	100	71	---
2327-2(A)	GS Silica	"	5% G-2 oil added to gum.	16 hrs. 400°F.	322	400	60	230
(B)				(A) + 6 hrs. 480°F.	373	57	72	---
2327-3(A)	GS Silica	"	10% G-2 oil added to gum.	16 hrs. 400°F.	241	275	62	230
(B)				(A) + 6 hrs. 480°F.	273	38	72	---
2327-4(A)	GS Silica	"	20% G-2 oil added to gum.	16 hrs. 400°F.	<25	<25	56	---
(B)				(A) + 6 hrs. 480°F.	223	25	67	---
2325(A)	GS Silica	25	10% G-2 oil added to pigment before milling.	16 hrs. 400°F.	<25	<25	70	---
				(A) + 6 hrs. 480°F.	150	<25	86	---
				(A) + 16 hrs. 480°F.	210	<25	86	---

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cured 15 min. at 230°F.; oven cure as indicated.

TABLE II-D-9

ADDITION OF VARIOUS PLASTICIZERS TO 25 VOL. GS SILICA STOCK

Compound No.	Pigment	Volume % Pigment	Plasticizer	Oven Cure	T	E	H
2381(A)	GS Silica	25	20% Tri-octyl phosphate	16 hrs. 400°F.	Brittle		92
(B)				(A) + 16 hrs. 480°F.			93
2381-1(A)	"	"	20% Tri-cresyl phosphate	16 hrs. 400°F.	Brittle		88
(B)				(A) + 16 hrs. 480°F.			92
2381-2(A)	"	"	20% Tri-octyl phthalate	16 hrs. 400°F.	Brittle		92
(B)				(A) + 16 hrs. 480°F.			92
2381-3(A)	"	"	20% HT-511	16 hrs. 400°F.	Brittle		80
(B)				(A) + 16 hrs. 480°F.			87
2381-4(A)	"	"	20% Tri-butoxyethyl phosphate	16 hrs. 400°F.	Brittle		95
(B)				(A) + 16 hrs. 480°F.			92
2381-5(A)	"	"	20% Di-butylsebacate	16 hrs. 400°F.	Brittle		93
(B)				(A) + 16 hrs. 480°F.			95
2381-6(A)	"	"	20% Flexol 360	16 hrs. 400°F.	Brittle		90
(B)				(A) + 16 hrs. 480°F.			95

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cure as indicated.

subsequent stabilization with glycerol. G-2 oil has a molecular weight of the order of 5000, and thus contains more active groups in the form of hydroxyl than does regular silicone oil. It was postulated that these hydroxyl groups might absorb some of the curing activity of GS silica, and thus render the stock more stable thermally. Table II-D-8 gives results of cures using up to 20 percent G-2 oil in a 15 volume GS stock. In compound #2325 the oil was first mixed with the pigment at 25 volume loading. In no case was any plasticizing action or increased high temperature stability observed with these compositions. Again, this oil like the silicone oil tended to produce a more brittle stock.

Additional tests were made using some of the better hydrocarbon rubber plasticizers with a 25 volume GS silica stock. These included phosphates, phthalates, sebacates and high molecular weight alcohols. Results in Table II-D-9 indicate that these materials, while compatible with silicone rubber, have an adverse effect on temperature resistance. In all cases brittle, high durometer stocks were formed after curing at 400 and 480°F.

Another method that was tried in order to soften highly cured GS silica stocks involved soaking the cured slabs in benzene solutions of silicone oil and

TABLE II-D-10

TREATING CURED GS SILICA STOCKS WITH PLASTICIZERS

Compound No.	Pigment	Volume % Pigment	Compounding Procedure	Oven Cure	T	E	H
2327(A)	GS Silica	15	Control	16 hrs. 480°F.	575	25	87
(B)	"	"	(A) Soaked 3 days in 10% solution LT-35 oil in benzene & dried	"	400	25	82
(C)	"	"	(A) Soaked 3 days in 10% solution SE-76 in benzene & dried.	"	No test. Slab cracked.		
2295-1(A)	GS Silica	25	Control	16 hrs. 480°F.	720	50	89
(B)	"	"	(A) Soaked in 10% solution SE-76 in benzene & dried slowly.	"	675	25	87
(C)	"	"	(B) Same, dried 24 hrs. @ 300°F.	"	745	25	90

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Stocks originally press cured 15 min. @ 230°F. and oven cured as indicated.

TABLE II-D-11

ACIDS AND FREE RADICAL INHIBITORS IN GS SILICA STOCK

Compound No.	Pigment	Volume % Pigment	Added Inhibitor	Oven Cure	T	E	H
2328-1	GS Silica	25	1% Stearic acid	(A) 16 hrs. @ 400°F.	582	38	90
				(B) (A) + 6 hrs. 480°F.	Brittle		92
-2	"	"	1% Benzoic acid	(A) 16 hrs. @ 400°F.	615	38	92
				(B) (A) + 6 hrs. 480°F.	Brittle		93
2329-1	GS Silica	25	1% Sodium nitrite	(A) 16 hrs. @ 400°F.	853	575	73
				(B) (A) + 6 hrs. 480°F.	512	25	90
-2	"	"	1% Quinoline	(A) 16 hrs. @ 400°F.	855	488	78
				(B) (A) + 6 hrs. 480°F.	408	6	90
-3	"	"	1% Sulfur	(A) 16 hrs. @ 400°F.	870	488	76
				(B) (A) + 6 hrs. 480°F.	Brittle		92
-4	"	"	1% Diphenyl amine	(A) 16 hrs. @ 400°F.	920	588	76
				(B) (A) + 6 hrs. 480°F.	Brittle		90

(1) General Electric SE-76 silicone gum used, no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cure as indicated.

gum. The solvent was found to swell these tightly cured slabs, allowing the oil or gum to penetrate. However, upon air or oven drying, the slabs cracked badly as they shrank during solvent evaporation. Tests on some of these slabs are given in Table II-D-10. It was apparent that these tightly cured stocks could not be distended through solvent swelling without rupturing the structure.

It has been proposed (Report #12) that the GS silica curing action may proceed through free radical formation induced as the coating breaks from the pigments. If high temperature overcuring is a result of too much cross-linking due to high free radical concentration, a free radical inhibitor might be expected to improve this situation. A number of compounds of this type were added in 1 percent amounts to a standard 25 volume GS silica batch; their effect on high temperature curing properties is given in Table II-D-11, compounds 2329(1-4). Physical properties were somewhat improved after a 400°F. cure, but curing at 480°F. produced slabs even more brittle than those with no inhibitor.

Compounds 2328(1-2) contained a small amount of stearic and benzoic acids respectively, to effect a slight depolymerization of the gum during oven curing. This might be expected to plasticize the stock effectively, but the two slabs tested show that the opposite proved

TABLE II-D-12

GS SILICA MIXED WITH OTHER PIGMENTS

Compound No.	Major Pigment	Minor Pigment	Oven Cure	T	E	H
2374	GS Silica (25 vol.)	None	(A) 16 hrs. 400°F.	907	388	83
			(B) (A) + 16 hrs. 480°F.	Brittle		94
2350	Santocel-C (15 vol.)	GS Silica (5 vol.)	(A) 16 hrs. 400°F.	146	25	68
			(B) (A) + 16 hrs. 480°F.	Brittle		
2374-1	GS Silica (15 vol.)	Alon (10 vols.)	(A) 16 hrs. 400°F.	Brittle		92
			(B) (A) + 16 hrs. 480°F.	Brittle		95
2384	GS Silica (10 vol.)	Alon (10 vols.)	(A) 1 hr. 300°F.	59	87	58
			(B) 24 hrs. 300°F.	152	67	63
			(C) 16 hrs. 400°F.	Cracked		65
2385	Alon (15 vol.)	GS Silica (5 vol.)	(A) 1 hr. 300°F.	Cracked		53
			(B) 24 hrs. 300°F.	Cracked		65
			(C) 16 hrs. 400°F.	Cracked		58

(1) General Electric SE-76 silicone gum used; no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cure as indicated.

to be the case.

Another method considered for controlling the tendency of GS silica to overcure was to dilute this pigment with non-active reinforcing fillers. Table II-D-12 gives data for varying amounts of Santocel C and Alon milled together with GS silica. Stocks of varying durometer were obtained, but it is apparent that this method is not satisfactory since the other pigment conflicts with the reinforcing structure of GS silica.

III. MECHANISM OF PEROXIDE VULCANIZATION OF HEXAMETHYL DISILOXANE

A. Statement of the Problem

Previous studies of the reaction of benzoyl peroxide with silicone rubber dissolved in solvent (n-heptane) enabled us to show that benzoic acid is produced, to the extent of about 20 percent of the total peroxide decomposed, but did not allow qualitative identification of other products of the reaction. This work has now been continued with chlorobenzoyl peroxide as the curing agent and pure hexamethyl disiloxane as the polymer to be cured.

B. Results

1. We find under the conditions used, 28 percent of the peroxide consumed results directly in benzoic acid, 50 percent of the peroxide decomposed with formation of chlorophenyl-substituted siloxanes and carbon dioxide, and 22 percent of the peroxide resulted in chlorobenzoyl-substituted siloxanes.

2. Sixteen percent of the hexamethyl disiloxane polymerized or cured as a result of the cross linking reaction. There was evidence that the higher molecular weight fractions were not only more highly cross-linked but also carried with them more of the chlorobenzoyl or chlorophenyl fragments. This might indicate secondary attack by the peroxide on the methylene groups previously combined with such fragments.

C. Introduction

Chlorobenzoyl peroxide can conceivably decompose in the presence of siloxanes in three basic ways as shown in the equations below:

1. $(ClC_6H_4COO)_2 \dashrightarrow 2\ ClC_6H_4COOH + $ one cross-link between siloxane chains.

In equation 1 chlorobenzoic acid has formed, the necessary hydrogens coming from the oxidation of the methyl groups on the siloxane chain. When two such oxidized methyl groups are adjacent, cross-links may be formed. It should be pointed out that a cross-link is not necessarily formed for every two molecules of benzoic acid that are formed because the necessary hydrogens may come from reactions 2 or 3.

2. $(ClC_6H_4COO)_2 \dashrightarrow 2\ CO_2 + 2\ ClC_6H_4CH_2$-siloxane $+ 2$ H.

Measurements of the carbon dioxide that is formed will show that reaction occurs according to equation 2 resulting in the formation of chlorophenyl substituted siloxanes.

3. $(ClC_6H_4COO)_2 \dashrightarrow 2\ ClC_6H_4COOCH_2$-siloxane $+ 2$ H.

The amount of reaction according to equation 3 can be determined by hydrolysis of the reaction products after extraction of free chlorobenzoic acid and analysis of the hydrolysate again for chlorobenzoic acid.

D. Introduction to Experimental Part

Acyl peroxides decompose under the influence of heat into free radicals which are able to react with suitably activated compounds. For example, benzoyl peroxide decomposes according to the following schemes[1,2,3]:

1. $(C_6H_5COO)_2 \dashrightarrow 2\ C_6H_5COO\cdot$

2. $C_6H_5COO\cdot \dashrightarrow C_6H_5\cdot + CO_2$

This type of reaction has been applied to the vulcanization of natural and synthetic rubbers, and particularly to the vulcanization of silicone polymers. The latter are generally represented with the following structure, where the methyl groups may be replaced by other alkyl or aryl groups:

$$\begin{array}{c} CH_3 \\ X{-}Si{-}O \\ CH_3 \end{array} \left[\begin{array}{c} CH_3 \\ {-}Si{-}O \\ CH_3 \end{array} \right]_n - \begin{array}{c} CH_3 \\ Si{-}X \\ CH_3 \end{array} \qquad \text{where } X = CH_3 \text{ or } OH$$

When an acyl peroxide is decomposed by heat in the presence of such a rubber, the peroxide radicals are able to react with the substituent groups on the silicone polymers. For example, when benzoyl peroxide is used to vulcanize silicone rubbers, it has been found that benzoic acid is formed during the reaction, and the following mechanisms can be postulated to explain the presence of the acid:

$$3.\quad \begin{array}{c} CH_3 \quad CH_3 \\ {-}Si{-}O{-}Si{-} \\ CH_3 \quad CH_3 \end{array} + C_6H_5COO. \dashrightarrow \begin{array}{c} CH_3 \quad CH_3 \\ {-}Si{-}O{-}Si{-} \\ \underset{\bullet}{CH_2} \quad CH_3 \end{array} + C_6H_5COOH$$

$$4.\quad \begin{array}{c} CH_3 \quad CH_3 \\ {-}Si{-}O{-}Si \\ CH_3 \quad \underset{\bullet}{CH_2} \end{array} + \begin{array}{c} CH_3 \quad CH_3 \\ {-}Si{-}O{-}Si \\ CH_3 \quad CH_3 \end{array} \dashrightarrow \begin{array}{c} CH_3 \quad CH_3 \\ {-}Si{-}O{-}Si{-} \\ CH_3 \quad CH_2 \end{array}{-}{-}{-}{-}\begin{array}{c} CH_3 \quad CH_3 \\ {-}Si{-}O{-}Si{-} \\ CH_2 \quad CH_3 \end{array} + H.$$

If this is a quantitatively accurate explanation, then all the benzoate radicals should result in the formation of benzoic acid. It was discovered, however, that the amount of benzoic acid isolated after vulcanization of silicone rubbers was only a fraction of the total yield of benzoic acid obtainable from the benzoyl peroxide used. It follows then that the fate of the various peroxide fragments is not a simple one and that other mechanisms must be operative during the vulcanization reaction.[4,5] Accordingly, an investigation was carried out to determine the fate of the peroxide fragments, the form that they assume in the presence of a silicone polymer and their role in the vulcanization reaction.

E. Method

The method used in this work was that employed by P.D. Bartlett and R. Altschul[6] in their study of peroxide induced polymerization of allyl compounds. The peroxide was p-chlorobenzoyl peroxide which was decomposed at moderate temperatures in the presence of hexamethyl disiloxane. The latter compound was chosen because of its similarity with silicone rubber polymers ordinarily used in industry; it could be considered the simplest silicone polymer molecule. The quantitative distribution of the various peroxide fragments in the reaction mixture was determined by tracing the chlorine tagged groups. Free p-chlorobenzoic acid was extracted from the reaction mixture and the amount of benzoate groups bound to the siloxane was determined by hydrolysis with strong alkali, freeing the acid which was then determined gravimetrically. The amount of phenyl fragments attached to the siloxane was estimated by the difference. Carbon dioxide evolved during the reaction was also determined gravimetrically, and found to be equivalent to the amount of phenyl substituent. The polymeric product was fractionally distilled under vacuum and the amount of aryl substituents attached to each fraction was determined by chlorine analysis.

F. Experimental Part

1. Materials used.

Hexamethyl disiloxane $(CH_3)_6Si_2O$ was prepared by hydrolyzing trimethyl chlorosilane $(CH_3)_3SiCl$ under mild conditions, condensing and fractionating the product (7); yield was 78.6 percent of theoretical, b.p. 100.2°C.; n_D^{20} was 1.3769 (reported: b.p. 100.5°C. n_D^{20} = 1.3774).

p-Chlorobenzoyl peroxide $(ClC_6H_4COO)_2$ was obtained by reacting sodium peroxide with p-chlorobenzoyl chloride (8) at 0 to 3°C. It was recrystallized from a mixture of methanol and chloroform. It decomposed violently at 138°C. When titrated by the iodometric method it assayed 99.67 percent peroxide.

2. Determination of the products of peroxide decomposition.

a. Description of reaction procedure.

A mixture containing hexamethyl disiloxane and p-chlorobenzoyl peroxide was refluxed at 90°C. under dry, carbon-dioxide-free nitrogen in a constant temperature bath until complete destruction of peroxide was assured (32 hours). Mechanical stirring was applied, employing a sealed stirrer. The carbon dioxide evolved during the reaction was collected in an Ascarite tube and dry, carbon-dioxide-free nitrogen was employed to flush the system until the Ascarite tube ceased to gain weight. The amount of carbon dioxide collected was 0.6163 grams.

b. Isolation of free p-chlorobenzoic acid.

At the end of the reaction period the liquid mixture had changed from colorless to light green and a solid precipitate had settled out. This was identified as p-chlorobenzoic acid. Three portions of a 10 percent aqueous solution of sodium bicarbonate were used to dissolve the precipitate and to extract any additional acidic compound dissolved in the mixture. Extraction was continued until no further precipitate was obtained on acidification. The combined alkaline solutions were boiled to eliminate traces of siloxane, filtered and acidified carefully with hydrochloric acid. The white suspension of p-chlorobenzoic acid that resulted was kept at 0°C. for 12 hours, filtered and washed with slightly acidic distilled water, dried and weighed. Melting point of the p-chlorobenzoic acid before recrystallization from alcohol was 238-240°C, after recrystallization it was

234-236°C. (reported 237-239°C.); the neutralization equivalent was 156.25 (the molecular weight of the monobasic acid is 156.57). Weight of the isolated acid was 1.235 grams.

c. Determination of total chlorine content in the reaction mixture.

The remaining liquid component (I) after removal of free p-chlorobenzoic acid was repeatedly washed with distilled water and dried over anhydrous magnesium sulfate. A sample of the purified liquid was analysed for chlorine by the Microchemical Laboratories of the Massachusetts Institute of Technology. The amount of chlorine found was 0.77 percent of the weight of the sample.

d. Hydrolysis of p-chlorobenzoate groups bound to siloxane chain to yield p-chlorobenzoic acid.

A sample of the purified liquid (I) weighing 1.3035 grams was dissolved in 5 cc of absolute methanol and 10 cc of 4.9 N sodium methoxide in methanol. The solution was refluxed at 90°C. for 12 hours. At the end of this period 30 cc.of distilled water was added to the solution, then 1.5 cc. of concentrated sulfuric acid and 80 more cc of distilled water. The mixture was extracted with four 50 cc portions of anhydrous ether and filtered. The extracts were combined, dried over anhydrous magnesium sulfate, the ether evaporated carefully and the resulting solid p-chlorobenzoic acid dried to constant weight. The melting point was 240-242°C. The weight of the isolated acid was 0.0134 grams.

e. Isolation of polymeric fractions from reaction mixture.

The remaining liquid (I) was fractionated under vacuum by Mr. J. L. Hecht of Yale University and several polymeric fractions were isolated. Three significant fractions were analysed for chlorine by the Microchemical Laboratories of the Massachusetts Institute of Technology, and the respective molecular weights were determined by the melting point depression technique.

3. Analysis of experimental results.

The reaction mixture consisted of 92.48 grams of hexamethyl disiloxane and 5.566 grams of p-chlorobenzoyl peroxide (6.02 percent by weight of siloxane), with a ratio of one mole of peroxide to 31.86 moles of siloxane. At the end of the reaction 0.6163 grams of carbon dioxide (38.15 percent of theoretical) and 1.235 grams of p-chlorobenzoic acid (22.045 percent of theoretical) were collected, according to the following reactions:

a. $(ClC_6H_4COO)_2 \xrightarrow{2H} 2\ ClC_6H_4COOH$

b. $(ClC_6H_4COO)_2 \longrightarrow 2\ ClC_6H_4\cdot + 2\ CO_2$

Table III-F-1 indicates the distribution of peroxide fragments in their different forms, as determined by calculations based on their chlorine contents. Two sets of product percentages were calculated, one based on the total chlorine present in the original peroxide and the other on the chlorine accounted for. Reading from the top of the table, the amount of chlorine present in the p-chlorobenzoyl peroxide initially used is recorded; then the chlorine attached to the p-chlorobenzoic acid (p-ClBA) isolated at the end of the reaction is reported (See Experimental part, paragraph 2 b). The amount of chlorine found by analysis of the reaction mixture after the removal of free p-chlorobenzoic acid follows. This corresponds to the total aryl substituents on the siloxane chain. The nature and the quantitative distribution of the above mentioned aryl substituents (involving phenyl and benzoate groups) on the siloxane chain is revealed by the next two lines. The chlorine content in the fourth line is that equivalent to the amount of carbon dioxide evolved through decarboxylation of p-chlorobenzoate groups and therefore corresponds to the amount of chlorophenyl groups present in the mixture (See reaction b above) and attached to the siloxane; the chlorine value in the fifth line indicates the amount of halogen present in the p-chlorobenzoic acid hydrolyzed from the mixture, and corresponds to the amount of hydrolyzable p-chlorobenzoate groups attached to the siloxane (See Experimental Part, paragraph 2 d).

TABLE III-F-1

DISTRIBUTION OF CHLORINE IN PARTIALLY VULCANIZED HEXAMETHYLDISILOXANE

	Weight in grams	percent based on total initial chlorine	percent based on total chlorine accounted for
Chlorine present in original peroxide	1.269	100.00	
Chlorine present in free isolated p-ClBA	0.2796	22.03	27.9
Chlorine found in reaction mixture after removal of free p-ClBA	0.7620	60.04	
Chlorine corresponding to total CO_2 evolved in original reaction	0.499	39.32	49.8
Chlorine present in chlorobenzoate groups hydrolyzed in second reaction	0.224	17.65	22.3
Chlorine present in substituents, total	0.723	56.97	
Chlorine unaccounted for, total	0.2664	20.92	
			100.0

In Table III-F-2 analyses of the polymeric fractions obtained by fractionation of the reaction mixture after removal of free p-chlorobenzoic acid are shown. The molecular weights were determined by melting point depression technique and the chlorine analyses were made by the Parr bomb fusion method.

The first line of the table shows the weight percent of the total isolated polymeric fractions based on the weight of the reaction mixture. Then the analysis of the first fraction follows, including molecular weight, chlorine content and molar ratio of chlorine to the isolated fraction. This treatment is applied to the other two fractions of increasing boiling point.

TABLE III-F-2

MOLECULAR WEIGHT OF PARTIALLY VULCANIZED HEXAMETHYLDISILOXANE

Weight percent of polymeric product based on reaction mixture	15.92
Molecular weight of fraction I	250
Chlorine in fraction I, percent	0.43
Molar ratio of chlorine to fraction I	0.036
Molecular weight of fraction II	855
Chlorine in fraction II, percent	4.47
Molar ratio of chlorine to fraction II	1.08
Molecular weight of fraction III	1060
Chlorine in fraction III, percent	7.86
Molar ratio of chlorine to fraction III	2.34

It is seen that the amount of polymers obtained by the experiment under discussion is only 15.92 percent of the weight of the reaction mixture. This low value, and the fact that only one mole of peroxide was present with 31.86 moles of siloxane, seem to indicate that the predominant mechanism of vulcanization does not proceed by a chain process, but rather by a stoichiometric reaction between the peroxide fragments and the activated siloxane. Further evidence is found when it is considered that a large molar excess of benzoyl peroxide is necessary to bring about vulcanization of silicone elastomers of high molecular weight.

Further examination of the values reported in Table III-F-II reveals that the chlorine content increases with increasing molecular weight; this fact might indicate that the substitution of one halogen containing aryl radical on a methyl group favors secondary attack which may result in a cross link and consequent formation of polymeric siloxanes.

G. Discussion

Reactions of acyl aryl peroxides under the influence of heat are generally considered from the viewpoint free radical formation. In our case, where p-chlorobenzoyl peroxide was studied, Equation 1 on page 36 can be broken down into the following reaction

$$(ClC_6H_4COO)_2 \dashrightarrow 2\ ClC_6H_4COO\cdot$$

which is then followed by the reaction of the activated chlorobenzoate groups with two adjacent methyl side chains of the siloxane molecule, splitting off hydrogens to form two molecules of chlorobenzoic acid and causing the formation of a cross linkage between the two methylene groups.

The free chlorobenzoate radicals can also react with the siloxane side chains forming addition products and liberating hydrogen atoms (Reaction 3, page 36). It is likely that both types of reaction occur as represented by reactions 1 and 3 on page 36. Another possibility is given by Reaction 2 on the same page, where carbon dioxide is liberated, with the formation of chlorophenyl addition products on the siloxane side chain[9,10].

An examination of the chlorine contents of the polymeric fractions shown in Table III-F-2 indicates that substitution on the siloxane molecule and cross-linking on the same molecule are occurring simultaneously. There is a good indication, based on the increased chlorine content of the heavier molecules, that cross-linking is encouraged because of the substitution of chlorophenyl or chlorobenzoate groups. It has been suggested that the remaining hydrogens on the substituted methyl group become increasingly active and thus react readily with a new molecule of peroxide forming a cross-link through the substituted group. This would account for the greater chlorine content of the more highly crosslinked polymers.

H. Conclusions

1. This work has shown that in addition to benzoic acid, which was known to be a product of the vulcanization of silicone rubbers by organic peroxides, a large amount

of substitution of the siloxane molecule occurs. In fact, substitution consumes 70-80 percent of the peroxide accounted for, with 20-30 percent appearing in the form of free benzoic acid.

2. Some of the substituted groups are benzoate groups and thus are a source of carbon dioxide which undoubtedly escapes during the oven curing of the rubber.

3. Substitution and cross-linking occur simultaneously in the same molecule and are probably related since more substitution occurred in the more highly cross linked molecules.

I. Bibliography

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IV. MECHANISM OF VULCANIZATION OF SILICONE RUBBER

A. Statement of the Problem

It has been shown in Progress Report No.10 (page 61) that benzoyl peroxide decomposes in a solvent alone or in solvent solution of silicone rubber to yield about 20 percent of benzoic acid and various other by-products not readily identified. In the previous section; it was found that 20 to 30 percent of the peroxide decomposes to form benzoic acid and the balance forms substitution products on the side methyl groups of the siloxanes. It was found, in Report No.11, page 9, that at concentrations below 2 percent of benzoyl peroxide in the rubber the effectiveness of the cross-linking reaction was 50 percent or more. This calculation was based on the formation of one cross-link per benzoyl peroxide molecule. It was of interest to see if the amount of benzoic acid by-product produced in the rubber during press curing was different from that produced in solution.

B. Results

1. The amount of benzoic acid formed is governed by the amount of benzoyl peroxide present. At initial concentrations of 6 percent or less only 4 to 10 percent of the benzoyl peroxide appeared as benzoic acid. This is much less than was found in experiments involving the reaction with silicone oils. With 8 percent of benzoyl peroxide added, 27 percent of it was transformed to benzoic acid.

Amount B.P. Present	Amount B.A. Found	Amount B.A. Found **
2 percent	.126 percent *	6.3
4 "	.242 "	6.05
6 "	.442 "	7.37
8 "	2.168 "	27.06

* percent based on 100 parts of rubber
** " " " B.P.

2. There is no systematic variation in amount of benzoic acid found as time and temperature are varied from 5 minutes below 212°F. to 10 minutes at 300°F.

3. Peroxide decomposition is 85 percent complete at all curing conditions more severe than a 10 minute rise to 250°F. plus 5 minutes at 250°F. Excellent cures were obtained with only 44 percent decomposition of the peroxide with a 10 minute rise to 250°F. followed by cooling to room temperature. Excellent cures were obtained with a 5 minute rise to 212°F. plus 10 minutes at 212°F. with only 41 percent decomposition of the peroxide. There seems to be no justification for curing longer or at a higher temperature.

C. Introduction

Methods were devised for removal from the cured slab and determination of (a) residual peroxide and (b) free benzoic acid. These determinations were made on a series of slabs containing various percentages of benzoyl peroxide and cured for various times and temperatures.

D. Experimental Part

Sixteen slabs were compounded using G.E. SE-76 gum, pre-heated Santocel C and varying percents of benzoyl peroxide, and given varying press cures. The cures ranged from five minutes rise to 212°F. to fifteen minutes rise to 300°F. plus ten minutes at 300°F. The press cured slabs were analyzed before oven curing for 1 hour at 300°F. A portion of each slab was cut into small pieces and refluxed with methanol to extract unreacted peroxide and benzoic acid. The peroxide was determined iodometrically and the benzoic acid electrochemically.

1. <u>Determination of a calibration curve for benzoic acid</u>

A method for the determination of benzoic acid in the extraction medium methanol was first established. A standard indicator end-point titration could not be used, so a potentiometric titration was employed. A standard was determin measuring the pH of prepared concentrations of benzoic acid, and the experimental amounts were found from the resulting calibration curve.

A 0.1_N solution of benzoic acid was prepared by dissolving 6.1 g. of dry benzoic acid in 500 ml. of methanol. A series of dilutions was made by pipetting samples from the stock 0.1_N solution, diluting to the desired concentration and measuring the pH for each solution. The pH versus concentration was plotted on semi-logarithmic paper and gave a straight line. A check was made on the points by preparing an exactly $.02_N$ solution of benzoic acid, measuring the pH, and determining concentration on the curve. Accuracy was within 0.5 percent.

2. <u>Determination of the acidity extracted from Santocel-C</u>

In previous work it was determined that Santocel-C is an acidic pigment. To determine whether the filler contributed any acidity to the extraction solution, three experiments were run by refluxing 4.39 g. of Santocel-C (the amount used in the compounding) with 300 ml. of methanol for two hours. The acidity of the extract was measured with caustic, and found to be negligible.

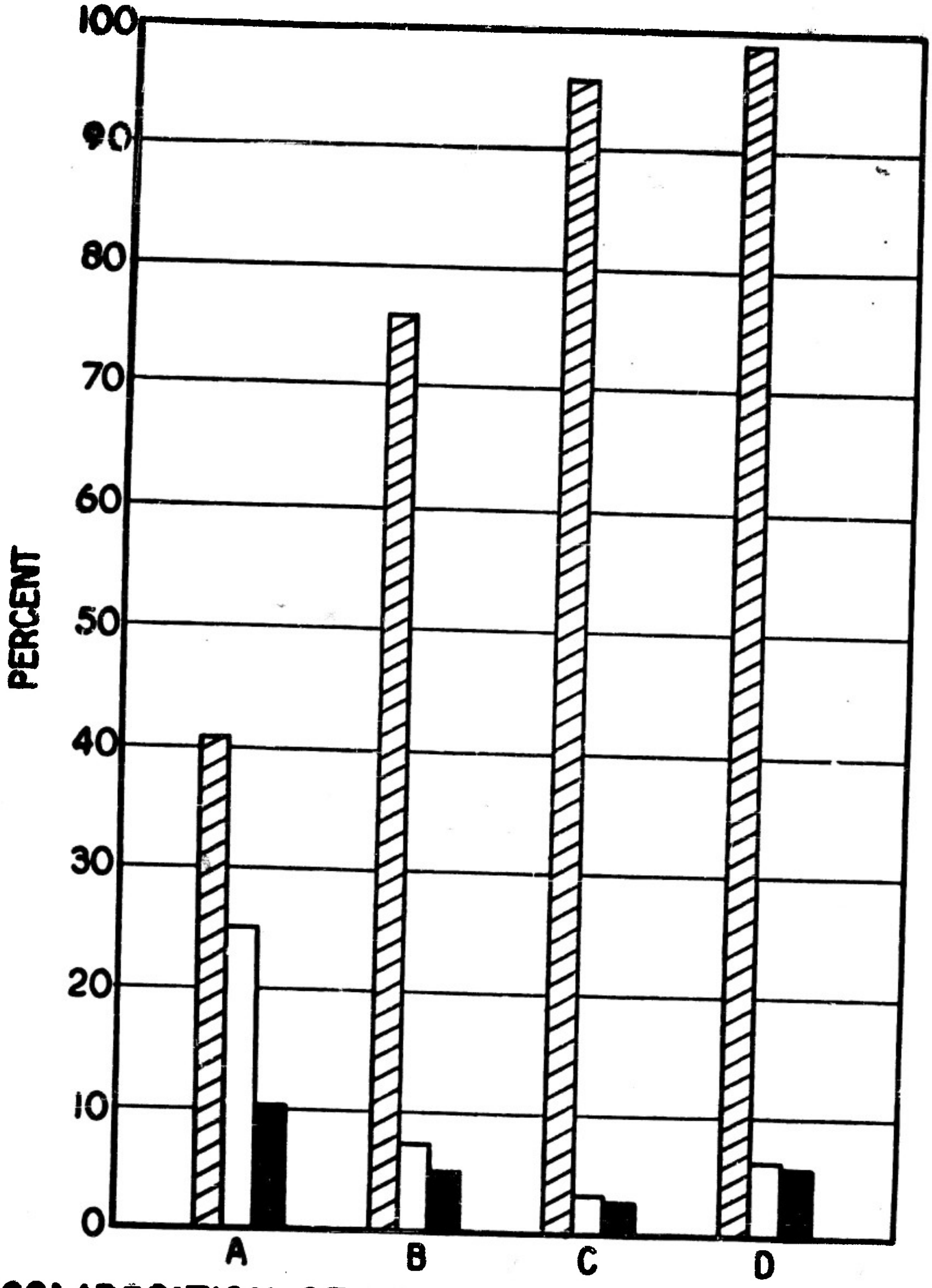
3. Extraction of benzoyl peroxide and benzoic acid from silicone rubber slabs having varying amounts of benzoyl peroxide and varying press cures.

The slab to be extracted was cut into small pieces and refluxed with 300 ml. of methanol until the maximum amount of benzoyl peroxide was found. The peroxide was determined by pipetting a sample from the reaction flask, adding an excess of NaI and 1 cc. of acetic acid, heating to the boiling point, and titrating with sodium thiosulfate. Another sample was pipetted from the reaction flask and a pH measurement taken, and the benzoic acid concentration was read from the pH calibration curve. As explained previously, the values found at the point of maximum peroxide concentration were the values used, as further extraction resulted in the thermal decomposition of the peroxide and the subsequent increase in the benzoic acid.

E. Discussion

The amount of benzoyl peroxide decomposed during press cures at various times and temperatures was

FIG. IV-A-1



DECOMPOSITION OF BENZOYL PEROXIDE VS. PRESS CURE

A 10' RISE TO 200°F. + 10' @ 200°F.
B 5' RISE TO 212°F. + 15' @ 212°F.
C 10' RISE TO 230°F. + 15' @ 230°F.
D 10' RISE TO 250°F. + 15' @ 250°F.

PEROXIDE DECOMPOSITION
BENZOIC ACID YIELD FROM DEC. PEROXIDE
BENZOIC ACID YIELD FROM TOTAL PEROXIDE

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA-44-109-QM-64

found to increase with time and the temperature. The peak of decomposition was reached at a press cure of ten minutes rise to 250°F. plus fifteen minutes at 250°F. (See Table IV-A-1 and Figure IV-A-1.)

While most of the study was confined to four percent concentration of benzoyl peroxide, some tests were made with 2, 6, and 8 percent. It was interesting to note that these latter concentrations gave poorer physical test results. It appears that a peroxide concentration greater than four results in a waste of curing agent. The theoretical yield of benzoic acid was calculated from the known amount of benzoyl peroxide compounded into the slab. With this calculated yield and the amount of benzoic acid found experimentally, the percent yield of benzoic acid was determined. Except for the slabs press cured in the lowest range of time and temperature, this percent yield was low.

As shown under Results, the amount of benzoic acid formed is a function principally of the amount of benzoyl peroxide present. Time and temperature play little part except that a larger proportion of the early decomposition of benzoyl peroxide goes to benzoic acid. With 8 percent of benzoyl peroxide present initially a larger proportion was transformed to benzoic acid also.

There seems to be no reason for long or high temperature press cures since good physical tests were obtained with short cures, even though the benzoyl

TABLE IV-A-1

Cpd.No.	%BP	Press Cure Min. °F.	BP before press cure gms.	Residual BP gms.	BA found gms.	Percentage of BP decomposed	Benzoic Acid Yield from dec. BP %	Benzoic Acid Yield from total BP %	Tensile p.s.i.	Elong. %	Hardness Shore A
									oven cured 1 hr.@ 300°F.		
2239-10 A	4	5' rise to 212	.513	.3385	.0355	34	20.9	6.87	196	200	
2431 B	4	10' rise to 200+10' @ 200	.502	.2958	.054	41	24.2	10.7	580	175	56
22391	4	10' rise to 250	.496	.22		44.5	no data taken		668	225	57
2239-11 C	4	5' rise to 212+10' @ 212	.510	.1215	.0300	76.2	7.67	5.84	715	228	45
2239-12 D	4	5' rise to 212+30' @ 212	.498	.0626	.0310	87.4	7.07	6.17	743	275	46
2239-2	4	10' rise to 230+5' @ 230	.493	.0958	.0340	80.55	8.1	6.36	615	200	
2239-3	4	10' rise to 230+10' @ 230	.493	.0923	.0250	81.25	6.15	5.05	555	212	55
2239-4 E	4	10' rise to 230+15' @ 230	.494	.0221	.0205	95.52	4.31	4.12	534	212	55
2239-5	4	10' rise to 250+5' @ 250	.502	.0480	.0290	90.44	6.34	5.72	658	225	58

TABLE IV-A-1 (Continued)

No.Cpd.	%BP	Press Cure	BP before press cure gms.	Res. BP gms.	BA found gms.	Dec. BP %	Benzoic Acid % yield from dec. BP.	Benzoic Acid % yield from total BP.	Tensile p.s.i.	Elong. %	Hardness Shore A
									Oven cured 1 hr.@ 300°F.		
2239-7	4	10' rise to 250 plus 10' at 250	.509	.0111	.0310	97.82	6.43	6.05	720	187	57
2239-14 F	4	10' rise to 250 plus 15' at 250	.483	.0074	.0350	98.47	7.26	7.20	718	213	57
2239-8	4	15' rise to 300 plus 5' at 300	.514	.01845	.0430	96.44	8.60	8.30	624	200	55
2239-9	4	15' rise to 300 plus 10' at 300	.519	.0184	.0315	96.5	6.21	6.04	690	175	60
2239-15	2	10' rise to 250 plus 10' at 250	.252	.0375	.0160	85.1	7.40	6.30	589	240	55
2239-16	6	10' rise to 250 plus 10' at 250	.73	.0258	.0648	96.41	9.13	7.37	550	144	60
2239-17	8	10' rise to 250 plus 10' at 250	.971	.0221	.265	97.72	27.7	27.06	462	150	63

TABLE IV A-2

OVEN CURING WITH VARYING PRESS CURES

Press cure	Oven cure	Tensile p.s.i.	Elongation per cent	Hardness Shore A
10' rise to 200°F. plus 10' @ 200°F.	1 hr. @ 300°F.	580	175	56
Same	24 hrs. @ 400°F.	473	100	65
5' rise to 212°F. plus 30' @ 212°F.	1 hr. @ 300°F.	743	275	46
Same	24 hrs. @ 400°F.	361	125	62
10' rise to 230°F. plus 15' @ 230°F.	1 hr. @ 300°F.	534	212	55
Same	24 hrs. @ 400°F.	481	175	60
10' rise to 250°F. plus 15' @ 250°F.	1 hr. @ 300°F.	718	213	57
Same	24 hrs. @ 400°F.	392	100	60

peroxide had not been completely decomposed. Nor is there any advantage of higher peroxide concentrations except to increase hardness and stiffness slightly. Pigment loading would be definitely cheaper.

Swelling studies report in Report No.11 indicated that 2 percent of benzoyl peroxide reacts to form cross links with an efficiency of 50 percent or more. Yet data reported here indicate benzoic acid formation occurs with an efficiency of 20 percent or less. Thus it would seem that cross links must be formed from some reaction other than No. 1 on Page 36. What this reaction may be is not known to us at this time. It would be interesting to study further the extraction of benzoic acid from pure silicone vulcanizates (uncompounded) and to determine the number of cross links on the same samples using the swelling technique used by Hauser in Report No.11. The data are shown in Table IV-A-1.

Table IV-A-2 shows the oven cure obtained in 24 hours at 400°F. Slabs with the least press cure actually gave the highest hardness after oven curing. This is probably caused by depolymerization under the influence of benzoic acid while the slabs were still in the press.

Such a study might make it possible to reconcile the divergent views expressed above. The expiration date of this contract makes it necessary to postpone further theoretical studies on the Mechanism of Benzoyl Peroxide Vulcanization of Silicone Rubber.

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